Supporting Information

Electrosynthesis of Benzoxazoles from *o*-Nitrophenols and Alcohols

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1. General Information

All reactions were performed using oven-dried glassware. Substrates and solvents were purchased from commercial sources (Adamas-beta and Aladdin) and used without further purification. Flash column chromatography was performed using silica gel (200-300 mesh, Tsingdao Haiyang Chemicals, China) with petroleum ether/ethyl acetate mixtures as the eluent. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (400 MHz) at room temperature using $CDCl_3$ as the solvent. Chemical shifts are reported in parts per million (ppm) relative to the residual solvent peak ($CDCl_3$: δ 7.26 for ^{1}H, δ 77.16 for ^{13}C) or tetramethylsilane (TMS, δ 0.00). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), or brs (broad singlet). Coupling constants (J) are reported in hertz (Hz). Gas chromatography analyses were carried out using two systems: (1) GC-MS was performed on a Thermo Scientific Trace 1300 GC/ISQ MS system equipped with an Agilent DB-WAX MS column (30 m × 0.25 mm × 0.25 μm) and helium as the carrier gas at 1.2 mL/min; the oven temperature program was set to 80 ℃ (hold 2 min), ramp to 245 ℃ at 10 ℃/min, then hold 3 min; the MS conditions were set as follows: ion source and transfer line temperatures 300 ℃, electron energy 70 eV, scan range m/z 50-600; (2) GC-FID analysis was conducted on an Agilent 7890B instrument using the same column type with helium as carrier gas; the oven program was 60 ℃ (hold 2 min), ramp to 245 ℃ at 10 ℃/min; the injector temperature was 245 ℃ with a pressure of 13.489 psi, total flow 24.2 mL/min, and septum purge flow 3.0 mL/min; the FID detector gases were set as follows: H_2 flow 30 mL/min, air flow 400 mL/min, and N_2 (makeup) flow 25 mL/min. High-resolution mass spectra (HRMS) were acquired using ESI on a Q-TOF mass spectrometer. Electrocatalytic reactions were performed in constant current mode using an HSPY-36-03 potentiostat. Cyclic voltammetry was carried out with a CHI760E electrochemical workstation (Shanghai Chenhua).

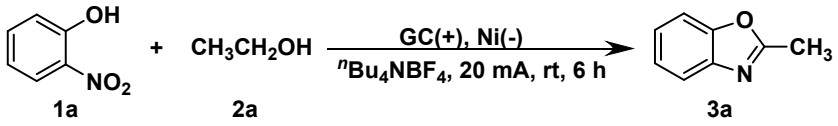
2. General Procedure for Electrosynthesis of Benzoxazoles from *o*-nitrophenols and alcohols.

In a custom-made Schlenk tube equipped with a magnetic stir bar, *o*-nitrophenol (1.0 mmol, 139.1 mg) and $^{n}Bu_4NBF_4$ (0.1 M, 263.4 mg) were dissolved in anhydrous ethanol (8.0 mL) under ambient atmosphere. Trifluoroacetic acid (10 mol%, 11.4 mg) was added, followed by the insertion of a glassy carbon plate (anode, 10 × 20 × 3 mm, immersed to 0.5 cm) and a nickel foam plate (cathode, 15 × 20 × 3 mm, immersed to 1.0 cm). The undivided electrochemical cell was operated under constant current (20 mA) at -10 °C for 8 h with vigorous stirring. A charge of 6 F/mol was applied to ensure complete substrate conversion while minimizing side reactions. After completion, the reaction mixture was warmed to reach room temperature and extracted with ethyl acetate (3 × 15 mL). The combined organic layers were washed with deionized water (15 mL) and saturated brine (2 × 15 mL), dried over anhydrous Na_2SO_4, filtered. The solvent was removed under reduced pressure, and the crude residue was analyzed by GC (using biphenyl as an internal standard) to determine the product yield. Finally, the product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, 6:1, v/v) to afford the desired product.

Figure S1. Photographic Guide for Electrochemical Reaction. Glassy carbon plate (anode, 10 × 20 × 3 mm), nickel foam plate (cathode, 15 × 20 × 3 mm), undivided electrochemical cell.

3. Optimization of Reaction Conditions for the Electrosynthesis of Benzoxazoles.

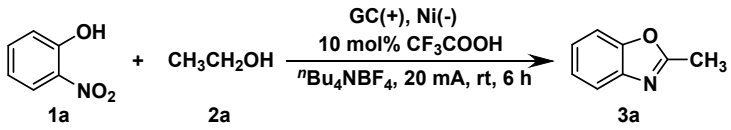
Table S1. Additional screening of electrode materials.[a]



Entry	Electrode	Electrolyte	Current	Catalyst	Yield/%[b]
1	GC/C	$^{n}Bu_4NBF_4$	20 mA	/	12
2	GC/GC	$^{n}Bu_4NBF_4$	20 mA	/	9
3	GC/Cu	$^{n}Bu_4NBF_4$	20 mA	/	10
4	GC/Al	$^{n}Bu_4NBF_4$	20 mA	/	Trace
5	GC/Pt	$^{n}Bu_4NBF_4$	20 mA	/	18
6	GC/Ni	$^{n}Bu_4NBF_4$	20 mA	/	28
7	GC/BDD	$^{n}Bu_4NBF_4$	20 mA	/	14
8	C/C	$^{n}Bu_4NBF_4$	20 mA	/	7
9	C/Pt	$^{n}Bu_4NBF_4$	20 mA	/	4
10	C/Ni	$^{n}Bu_4NBF_4$	20 mA	/	6
11	Pt/C	$^{n}Bu_4NBF_4$	20 mA	/	3
12	Pt/Pt	$^{n}Bu_4NBF_4$	20 mA	/	3

[a] Reaction conditions: **1a** (1 mmol), $^{n}Bu_4NBF_4$ (0.1 M), **2a** (8 mL), glassy carbon (GC) anode (10 × 20 × 3 mm), nickel (Ni) cathode (15 × 20 × 3 mm), constant current 20 mA, room temperature, 6 h. [b] Yield determined by GC using biphenyl as the internal standard.

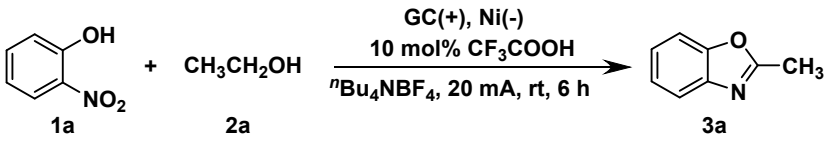
Table S2. Screening of Reaction slovents.[a]



Entry	Electrode	Electrolyte	Current	Solvent	Yield/%[b]
1	GC/Ni	$^{n}Bu_4NBF_4$	20 mA	/	28
2	GC/Ni	$^{n}Bu_4NBF_4$	20 mA	EtOH/DMF	trace
3	GC/Ni	$^{n}Bu_4NBF_4$	20 mA	EtOH/H_2O	9
4	GC/Ni	$^{n}Bu_4NBF_4$	20 mA	EtOH/DMSO	10

[a] Reaction conditions: **1a** (1 mmol), $^{n}Bu_4NBF_4$ (0.1 M), **2a** (8 mL), glassy carbon (GC) anode (10 × 20 × 3 mm), nickel (Ni) cathode (15 × 20 × 3 mm), constant current 20 mA, room temperature, 6 h. [b] Yield determined by GC using biphenyl as the internal standard.

Table S3. Additional screening of reaction temperature.[a]



Entry	Electrode	Electrolyte	Temperature/°C	Yield/%[b]
1	GC/Ni	$^{n}Bu_4NBF_4$	r.t.	40
2	GC/Ni	$^{n}Bu_4NBF_4$	0	51
3	GC/Ni	$^{n}Bu_4NBF_4$	-10	56
4	GC/Ni	$^{n}Bu_4NBF_4$	-20	47
5	GC/Ni	$^{n}Bu_4NBF_4$	-30	40

[a] Reaction conditions: **1a** (1 mmol), $^{n}Bu_4NBF_4$ (0.1 M), **2a** (8 mL), glassy carbon (GC) anode (10 × 20 × 3 mm), nickel (Ni) cathode (15 × 20 × 3 mm), constant current 20 mA, room temperature, 6 h. [b] Yield determined by GC using biphenyl as the internal standard.

4. Scale-up Experiment

In a 50 mL Schlenk tube equipped with a magnetic stir bar, *o*-nitrophenol (5 mmol, 695.5 mg) and $^{n}Bu_4NBF_4$ (0.1 M, 658.5 mg) were dissolved in anhydrous ethanol (20.0 mL) under ambient atmosphere. Trifluoroacetic acid (10 mol%, 114 mg) was added, followed by insertion of a glassy carbon plate (anode, 10 × 20 × 3 mm, immersed to 0.5 cm) and a nickel foam plate (cathode, 15 × 20 × 3 mm, immersed to 1.0 cm). The undivided electrochemical cell was operated under constant current (20 mA) at -10 ℃ with vigorous stirring. The reaction progress was monitored via interval sampling until the voltage stabilized and the **3a** yield remained unchanged (33 h). Upon completion, the reaction mixture was extracted with EtOAc (3 × 30 mL), and the combined organic layers were washed with deionized water (30 mL) and saturated aqueous NaCl solution (30 mL, 2 times) to remove residual electrolytes and water-soluble impurities. After drying over anhydrous Na_2SO_4, the solution was concentrated under reduced pressure. The crude product was purified by flash column chromatography (petroleum ether/ethyl acetate, 6:1, v/v) to afford the desired product.

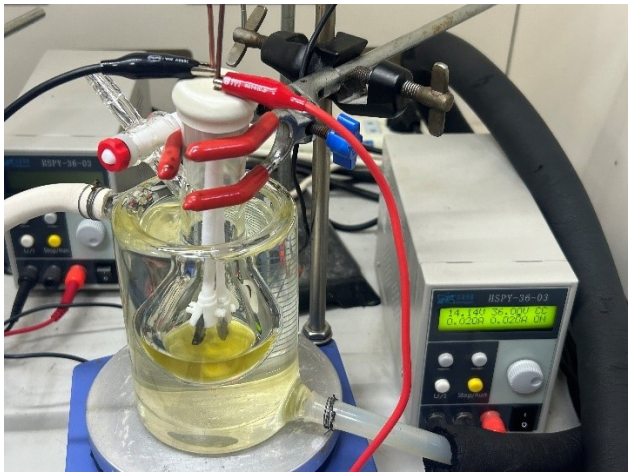


Figure S2. Diagram of the reaction device for scale-up experiment.

5. Radical Capture Experiment

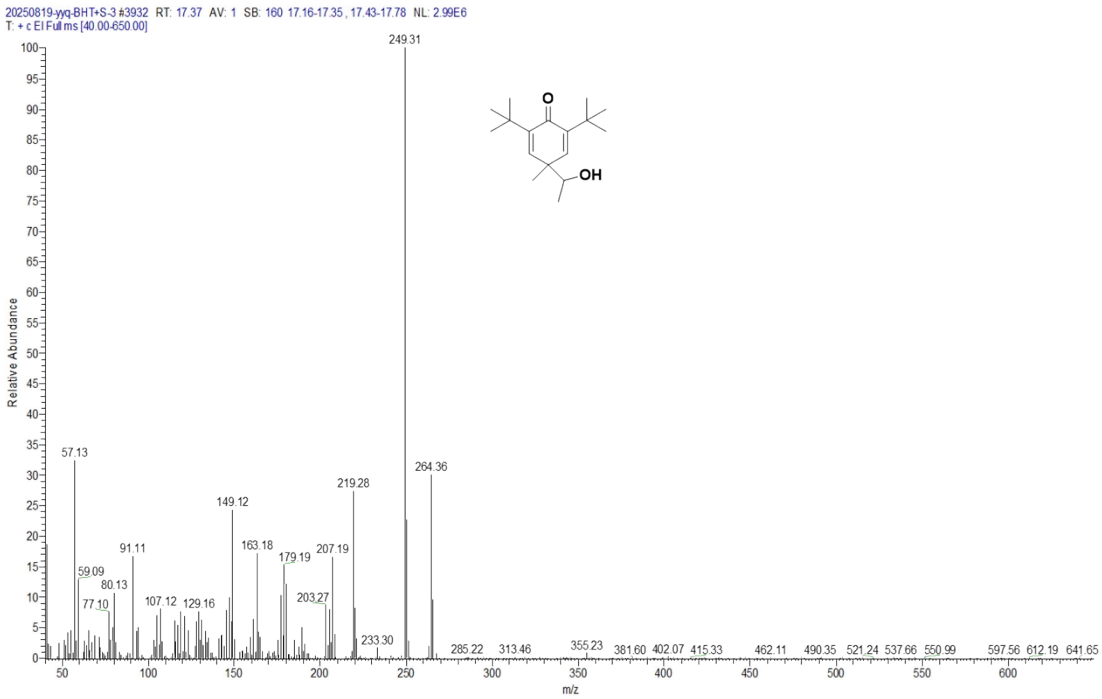


Figure S3. GC-MS of BHT-radical adduct

6. H-Cell Based Electrochemical Oxidative Cyclization Reaction

Electrochemical reactions were performed in an H-cell equipped with a Nafion N117 membrane. The membrane was pre-treated by heating sequentially in 3% H_2O_2 (aq) at 80 ℃ for 1 h (to remove organic contaminants), in 5% H_2SO_4 (aq) at 80 ℃ for 1 h (to protonate the sulfonic acid groups), and in ultrapure H_2O at 80 °C for 0.5 h, followed by storage in ultrapure H_2O at 4 °C prior to use. The anodic compartment contained a solution of $^{n}Bu_4NBF_4$ (0.1 M) in acetonitrile (6.5 mL) and benzyl alcohol (1.5 mL) with TFA (10 mol %), and the cathodic compartment contained *o*-nitrophenol (1.0 mmol) and $^{n}Bu_4NBF_4$ (0.1 M) in acetonitrile (8 mL) with TFA (10 mol %). Both compartments were then subjected to constant current electrolysis at 20 mA for 8 h at room temperature (Figure S4).

Figure S4. Electrochemical reaction in divided cell. Reaction conditions: benzyl alcohol (1.5 ml), TFA (10 mol %), $^{n}Bu_4NBF_4$ (0.1 M), CH_3CN (6.5 mL) in anodic compartment, *o*-nitrophenol (1.0 mmol), TFA (10 mol %), $^{n}Bu_4NBF_4$ (0.1 M), and CH_3CN (8 mL) cathodic compartment, H-cell with Nafion N117 membrane, constant current 20 mA, room temperature, 8 h.

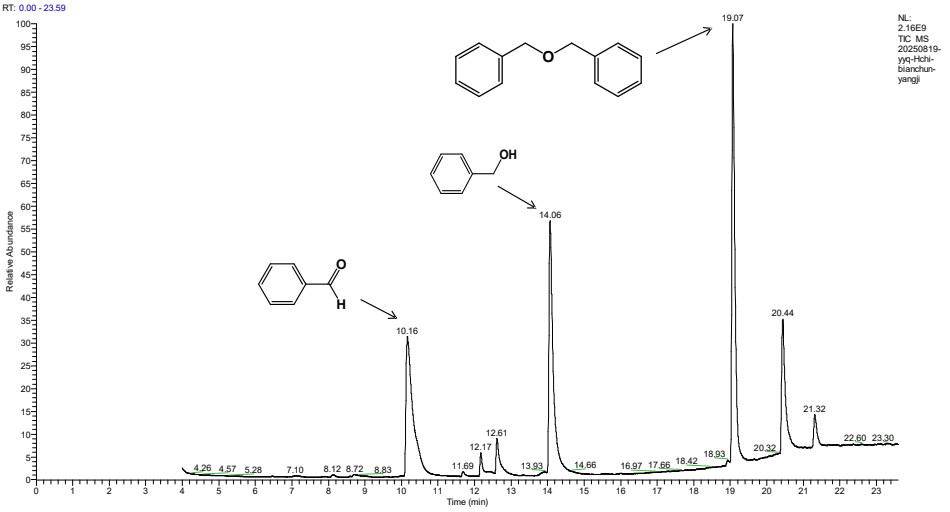


Figure S5. GC analysis of anodic compartment

7. Cyclic Voltammetry Experiment

Cyclic voltammetry (CV) measurements were conducted on a CHI760E electrochemical workstation (Shanghai Chenhua Instrument Plant, China) at room temperature under an inert atmosphere using a Schlenk line. A conventional three-electrode cell was employed, consisting of a glassy carbon working electrode (polished with 0.05 μm alumina slurry, rinsed with deionized water, sonicated for 5 min, and dried under nitrogen), a platinum plate counter electrode (electrochemically cleaned by cycling in the supporting electrolyte at 1 V/s until stable), and an Ag/AgCl reference electrode (3 M KCl). The electrolyte was 10 mL of CH_3CN containing 0.5 mmol $^nBu_4NBF_4$. CV scans were recorded at a scan rate of 200 mV/s from 0.0 to 3.0 V (vs. Ag/AgCl), with a sampling interval of 0.001 V and a sensitivity of 0.1 A/V. All curves are plotted following IUPAC conventions. Specific experimental parameters corresponding to each curve are provided in the figure captions.

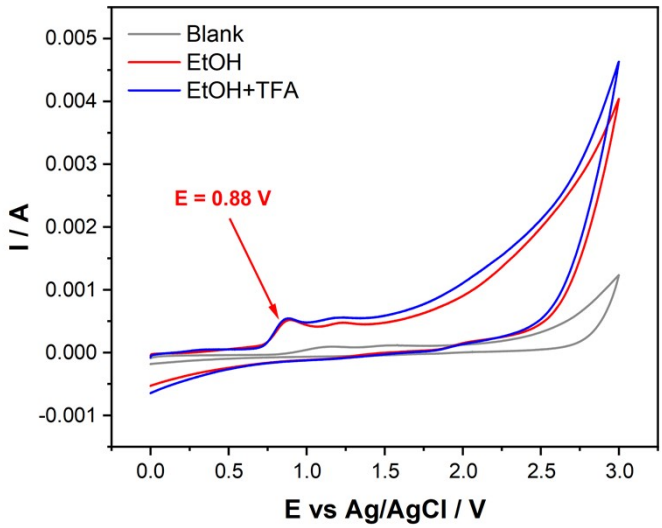


Figure S6. Cyclic voltammetry of ethanol in CH_3CN solvent and $^nBu_4NBF_4$ as the electrolyte. Glassy carbon, Pt, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The scan rate is 0.2 V/s. Gray: $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); red: EtOH (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); blue: EtOH (0.05 mmol), TFA (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL).

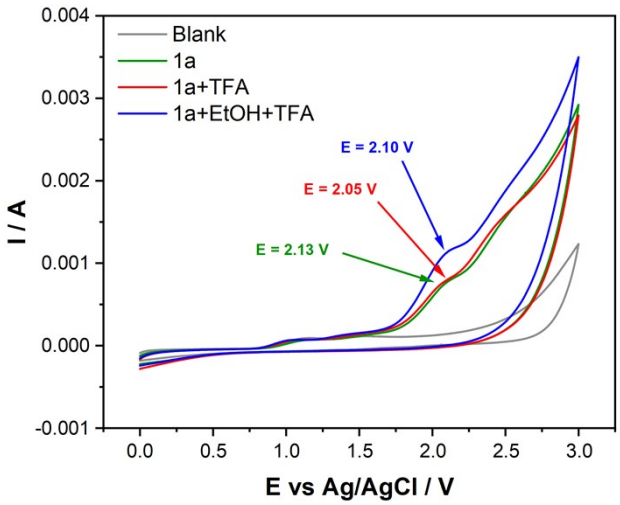


Figure S7. Cyclic voltammetry of related compounds in CH_3CN solvent and $^nBu_4NBF_4$ as the electrolyte. Glassy carbon, Pt, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The scan rate is 0.2 V/s. Gray: $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); green: **1a** (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); red: **1a** (0.05 mmol), TFA (0.05mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); blue: **1a** (0.05 mmol), EtOH (0.05mmol), TFA (0.05mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL).

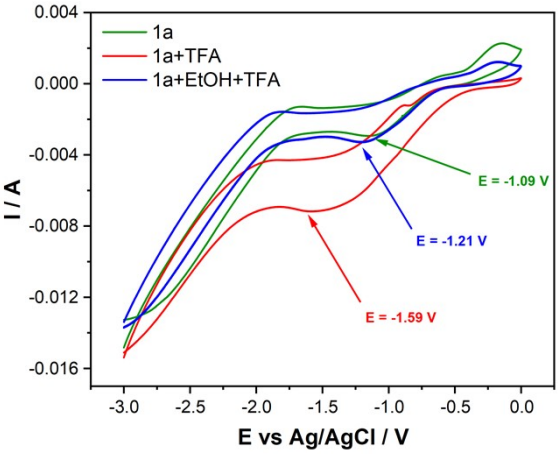


Figure S8. Cyclic voltammetry of **1a** in the negative direction. Glassy carbon, Pt, and Ag/AgCl were used as the working electrode, counter electrode, and reference electrode, respectively. The scan rate is 0.2 V/s. Green: **1a** (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); Red: **1a** (0.05 mmol), TFA (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL); Blue: **1a** (0.05 mmol), EtOH (0.05 mmol), TFA (0.05 mmol), $^nBu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL).

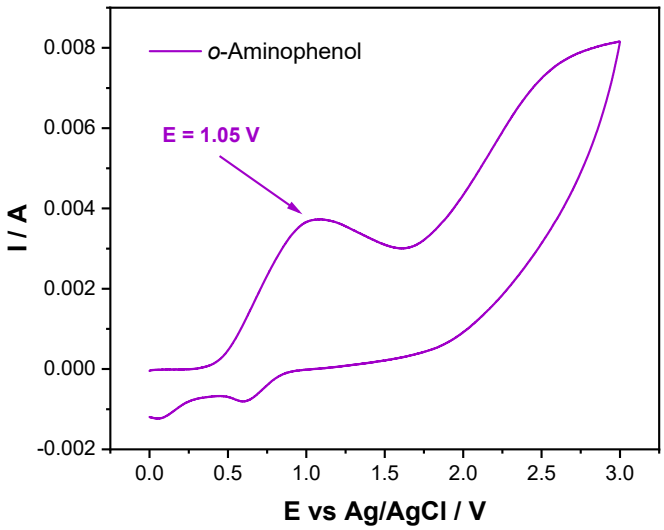
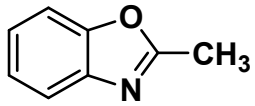


Figure S9. Cyclic voltammetry of *o*-aminophenol in CH_3CN solvent and $^{n}Bu_4NBF_4$ as the electrolyte. Glassy carbon, Pt and Ag/AgCl were used as the working electrode, counter electrode and reference electrode, respectively. Cyclic voltammetry was performed at ambient temperature. The scan rate is 0.2 V/s, ranging from 0 V to 3 V. Purple: *o*-Aminophenol (0.05 mmol), $^{n}Bu_4NBF_4$ (0.5 mmol), CH_3CN (10 mL).

We performed the CV experiment of *o*-aminophenol (**1a'**) and obtained its oxidation potential at 1.05 V *vs* Ag/AgCl (Fig S8), so it is difficult to oxidize compared to ethanol.

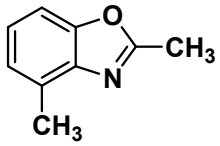
8. Characterization of Products

2-Methylbenzoxazole(3a)[1]



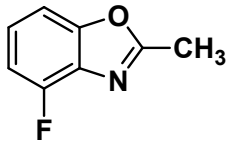
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 97.2 mg, 73% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (m, *J* = 7.3 Hz, 1H), 7.30 (m, *J* = 8.0 Hz, 1H), 7.18-7.07 (m, 2H), 2.46 (s, 3H). **^{13}C NMR: (101 MHz, $CDCl_3$)** δ 163.9, 151.0, 141.1, 124.5, 124.2, 119.0, 110.3, 14.6. **GC-MS** m/z(%): 132.59(96)$[M]^{+\cdot}$, 104.09(100), 92.07(45), 78.10(74).

2,4-Dimethylbenzoxazole(3b)[1]



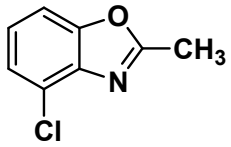
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 79.5 mg, 54% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 1H), 2.63 (s, 3H), 2.59 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.1, 150.8, 140.7, 129.8, 124.8, 124.2, 107.6, 16.6, 14.6. **GC-MS** m/z (%): 147.10(100)$[M]^{+\cdot}$, 118.08(15), 106.10(24), 78.09(57).

4-Fluoro-2-methylbenzoxazole(3c)



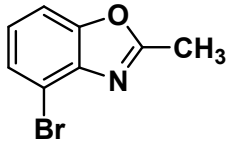
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 67.9 mg, 45% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.29-7.19 (m, 2H), 7.04-6.98 (m, 1H), 2.64 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.2, 154.4, 153.3 (d, *J* = 7.5 Hz), 151.8, 124.9 (d, *J* = 7.2 Hz), 110.5 (d, *J* = 17.7 Hz), 106.5 (d, *J* = 4.5 Hz), 14.6. **GC-MS** m/z (%): 151.10(100)$[M]^{+\cdot}$, 122.08(24), 96.07(22), 82.07(25). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -125.06. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for C_8H_7NOF:152.0512, found: 152.0516.

4-Chloro-2-methylbenzoxazole(3d)[2]



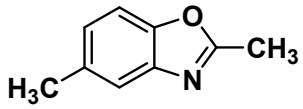
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 61.8 mg, 37% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 8.0 Hz, 1H), 2.67 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.8, 151.7, 139.4, 125.1, 124.5, 124.1, 109.0, 14.7. **GC-MS** m/z (%): 167.07(100)$[M]^{+\cdot}$, 169.09(33)$[M+2]^{+\cdot}$, 104.09(27), 63.06(28).

4-Bromo-2-methylbenzoxazole(3e)[2]



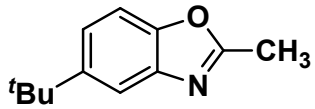
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 63.3 mg, 30% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (dd, *J* = 18.1, 8.1 Hz, 2H), 7.17 (t, *J* = 8.1 Hz, 1H), 2.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 151.1, 141.0, 127.4, 125.6, 112.0, 109.6, 14.7. **GC-MS** m/z (%): 211.01(100)$[M]^{+\cdot}$, 213.03(92)$[M+2]^{+\cdot}$, 132.10(44), 106.07(22), 104.08(20), 63.06(42).

2,5-Dimethylbenzoxazole(3f)[1]



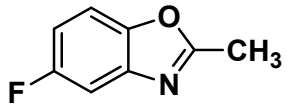
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 75.1 mg, 51% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.42 (s, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 10.0 Hz, 1H), 2.61 (s, 3H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0, 149.3, 141.9, 134.0, 125.6, 119.5, 109.6, 21.5, 14.7. **GC-MS** m/z (%): 147.13(100)$[M]^{+\cdot}$, 106.08(32), 78.09(63).

5-(*tert*-butyl)-2-methylbenzoxazole(3g)[3]



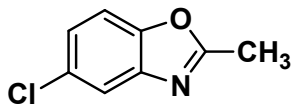
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 71.9 mg, 38% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.66 (s, 1H), 7.42-7.30 (m, 2H), 2.61 (s, 3H), 1.37 (s, 9H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.0, 149.1, 147.8, 141.6, 122.2, 116.1, 109.4, 35.0, 32.0, 14.7. **GC-MS** m/z (%): 189.17(20)$[M]^{+\cdot}$, 174.14(100)$[M\text{-}CH_3]^{+\cdot}$, 146.10(20), 133.13(19), 105.11(16).

5-Fluoro-2-methylbenzoxazole(3h)[1]



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 81.6 mg, 54% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.44-7.22 (m, 2H), 7.01 (t, *J* = 9.1 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.8, 158.8, 147.4, 142.4 (d, *J* = 13.0 Hz), 112.0, 110.5 (d, *J* = 10.1 Hz), 106.3 (d, *J* = 25.6 Hz), 14.8. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -118.59. **GC-MS** m/z (%): 151.09(100)$[M]^{+\cdot}$, 122.06(24), 96.06(25), 82.06(46), 81.07(16).

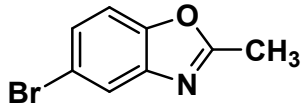
5-chloro-2-methylbenzoxazole(3i)[1]



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 55.2 mg,

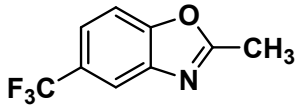
33% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 2.5 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.21-7.15 (m, 1H), 2.56 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.4, 149.6, 142.8, 129.7, 124.8, 119.5, 111.0, 14.7. **GC-MS** m/z (%): 167.02(100)$[M]^{+\cdot}$, 169.05(29)$[M+2]^{+\cdot}$, 104.06(36), 98.02(21), 63.05(35).

5-bromo-2-methylbenzoxazole(3j)[1]



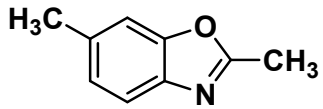
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 52.8 mg, 25% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.69 (d, J = 8.2 Hz, 1H), 7.34-7.21 (m, 2H), 2.56 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 150.0, 143.2, 127.6, 122.6, 116.9, 111.5, 14.7. **GC-MS** m/z (%): 211.00(100)$[M]^{+\cdot}$, 213.03(93)$[M+2]^{+\cdot}$, 104.10(45), 91.12(16), 63.04(63).

5-trifluoromethyl-2-methylbenzoxazole(3k)



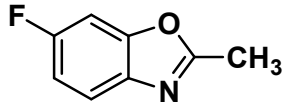
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 40.2 mg, 20% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.54 (s, 2H), 2.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.8, 152.8, 141.8, 127.0 (q, *J* = 32.8 Hz), 123.0, 121.9 (d, *J* = 3.7 Hz), 117.2 (d, *J* = 4.1 Hz), 110.7, 14.6. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -60.94. **GC-MS** m/z (%): 201.10(100)$[M]^{+\cdot}$, 132.07(16), 104.07(21), 63.05(24). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_9H_7NOF_3$:202.0484, found: 202.0480.

2,6-dimethylbenzoxazole(3l)[1]



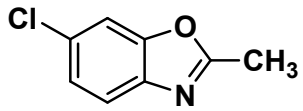
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 73.5 mg, 50% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.50 (d, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 1.8 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 2.61 (s, 3H), 2.46 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.4, 151.4, 139.4, 134.9, 125.4, 118.9, 110.5, 21.8, 14.6. **GC-MS** m/z (%): 147.09(100)$[M]^{+\cdot}$, 118.07(15), 106.07(30), 78.08(62).

6-fluoro-2-methylbenzoxazole(3m)[1]



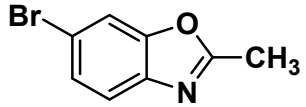
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 78.6 mg, 52% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (dd, *J* = 9.8, 4.9 Hz, 1H), 7.19 (d, *J* = 9.3 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 1H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 159.2, 151.1, 137.9, 119.8 (d, *J* = 10.1 Hz), 112.0 (d, *J* = 24.5 Hz), 98.6 (d, *J* = 28.1 Hz), 14.6. **^{19}F NMR (470 MHz, $CDCl_3$)** δ -116.42. **GC-MS** m/z (%): 151.07(100)$[M]^{+\cdot}$, 122.04(29), 96.05(31), 82.04(26), 81.02(18).

6-chloro-2-methylbenzoxazole(3n)[4]



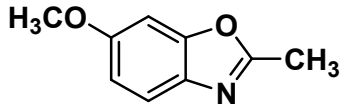
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 63.5 mg, 38% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 2.2 Hz, 1H), 7.29 (d, *J* = 2.8 Hz, 1H), 2.63 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.7, 151.2, 140.4, 130.3, 124.9, 120.0, 111.0, 14.7. **GC-MS** m/z (%): 167.03(100)$[M]^{+\cdot}$, 169.02(32)$[M+2]^{+\cdot}$, 104.04(57), 63.02(37).

6-bromo-2-methylbenzoxazole(3o)[5]



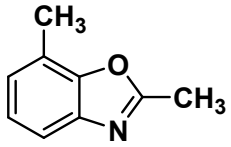
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 61.3 mg, 29% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.63 (s, 1H), 7.56-7.34 (m, 2H), 2.62 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.6, 151.5, 140.8, 127.6, 120.5, 117.5, 113.9, 14.6. **GC-MS** m/z (%): 210.99(96)$[M]^{+\cdot}$, 212.97(100)$[M+2]^{+\cdot}$, 104.06(82), 77.07(17), 63.03(53).

6-methoxy-2-methylbenzoxazole(3p)[1]



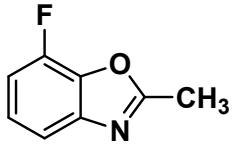
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 70.2 mg, 43% yield. Brown oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.49 (d, *J* = 8.8 Hz, 1H), 6.98 (d, *J* = 2.5 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.82 (s, 3H), 2.58 (s, 3H).. **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.9, 157.8, 151.8, 135.2, 119.4, 112.1, 95.4, 56.0, 14.6. **GC-MS** m/z (%): 163.05(96)$[M]^{+\cdot}$, 148.04(100)$[M\text{-}CH_3]^{+\cdot}$, 120.06(16), 106.07(32), 79.06(17), 51.03(19).

2,7-dimethylbenzoxazole(3q)[6]



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 80.9 mg, 55% yield. Yellow oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.46 (d, *J* = 7.9 Hz, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 2.63 (s, 3H), 2.50 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.6, 150.3, 141.2, 125.6, 124.1, 120.9, 116.8, 15.2, 14.7. **GC-MS** m/z (%): 147.11(100)$[M]^{+\cdot}$, 106.11(50), 78.09(48).

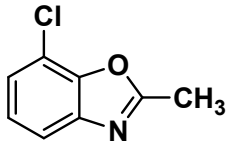
7-fluoro-2-methylbenzoxazole(3r)



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 62.0 mg, 41% yield. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.43 (d, *J* = 7.9 Hz, 1H), 7.23 (d, *J* = 4.6

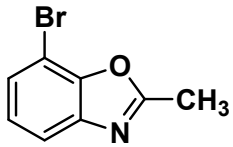
Hz, 1H), 7.05 (t, *J* = 9.1 Hz, 1H), 2.67 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.5, 148.2, 145.7, 144.9, 124.7 (d, *J* = 6.2 Hz), 115.3 (d, *J* = 4.1 Hz), 111.5 (d, *J* = 16.6 Hz), 14.56. **GC-MS** m/z (%): 151.09(100)$[M]^{+\cdot}$, 129.10(31), 122.09(16), 101.10(45), 82.11(16). **^{19}F NMR (470 MHz, $CDCl_3$)** δ -134.78. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for C_8H_7NOF:152.0512, found: 152.0509.

7-chloro-2-methylbenzoxazole(3s)[7]



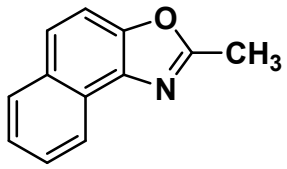
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 65.2 mg, 39% yield. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.29-7.24 (m, 1H), 7.21 (t, *J* = 7.9 Hz, 1H), 2.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.4, 147.6, 142.8, 125.0, 125.0, 118.1, 115.6, 14.6. GC-MS m/z (%): 167.06(100)$[M]^{+\cdot}$, 169.06(33)$[M+2]^{+\cdot}$, 104.09(31), 98.06(15), 63.05(33). **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for C_8H_7NOCl:168.0216, found: 168.0219.

7-bromo-2-methylbenzoxazole(3t)[7]



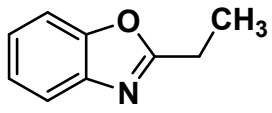
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 65.4 mg, 31% yield. White solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.56 (d, J = 7.9 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.16 (t, J = 7.9 Hz, 1H), 2.66 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 164.2, 149.2, 142.2, 127.7, 125.4, 118.6, 102.2, 14.7. **GC-MS** m/z (%): 211.00(96)$[M]^{+\cdot}$, 213.03(100)$[M+2]^{+\cdot}$, 132.08(21), 104.09(42), 63.06(48).

2-methylnaphth[1,2-*d*]oxazole(3u)[8]



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 87.9 mg, 48% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.46 (d, *J* = 7.3 Hz, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 1H), 7.66-7.56 (m, 2H), 7.53-7.47 (m, 1H), 2.70 (s, 3H) **^{13}C NMR (101 MHz, $CDCl_3$)**δ 162.8, 148.1, 136.5, 131.0, 128.5, 126.9, 126.2, 125.3, 125.1, 121.9, 110.6, 14.6. **GC-MS** m/z (%): 183.14(100)$[M]^{+\cdot}$, 154.12(36), 128.11(16), 114.10(32).

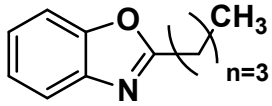
2-ethylbenzoxazole(3aa)[9]



Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 80.4 mg, 55% yield. Colourless oil. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.73-7.60 (m, 1H), 7.56-7.38 (m, 1H),

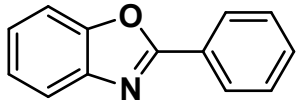
7.35-7.18 (m, 2H), 3.01-2.86 (m, 2H), 1.45 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.2, 150.9, 141.5, 124.5, 124.2, 119.7, 110.4, 22.3, 11.0. **GC-MS** m/z (%): 146.11(100) $[M]^{+\cdot}$, 132.09(16)$[M\text{-}CH_3]^{+\cdot}$, 63.05(17).

2-butylbenzoxazole(3ab)[9]



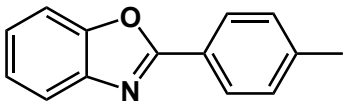
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 6:1), 105.1 mg, 60% yield. Yellow solid. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.62 (d, *J* = 9.3 Hz, 1H), 7.40 (d, *J* = 9.3 Hz, 1H), 7.25-7.17 (m, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 1.81 (p, *J* = 7.6 Hz, 2H), 1.39 (h, *J* = 7.4 Hz, 2H), 0.91 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.2, 150.7, 141.4, 124.3, 123.9, 119.4, 110.1, 28.7, 28.2, 22.2, 13.6. **GC-MS** m/z (%): 175.16(6)$[M]^{+\cdot}$, 160.15(4)$[M\text{-}CH_3]^{+\cdot}$, 146.10(26)$[M\text{-}CH_2CH_3]^{+\cdot}$, 133.10(100)$[M\text{-}CH_2CH_2CH_3]^{+\cdot}$.

2-phenylbenzoxazole(3ac)[1]



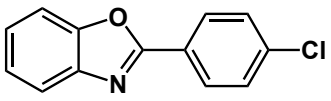
Purified by flash column chromatography (eluent: petroleum ether/ethyl acetate = 10:1), 157.6 mg, 82% yield. White soild. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.27 (dd, *J* = 6.7, 3.2 Hz, 2H), 7.83-7.73 (m, 1H), 7.62-7.55 (m, 1H), 7.55-7.47 (m, 3H), 7.40-7.30 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.1, 150.9, 142.2, 131.6, 129.0, 127.7, 127.3, 125.2, 124.6, 120.1, 110.7. **GC-MS** m/z (%): 192.12(100)$[M]^{+\cdot}$, 167.12(27), 77.07(16), 63.05(29).

2-(4-methylphenyl)benzoxazole(3ad)[10]



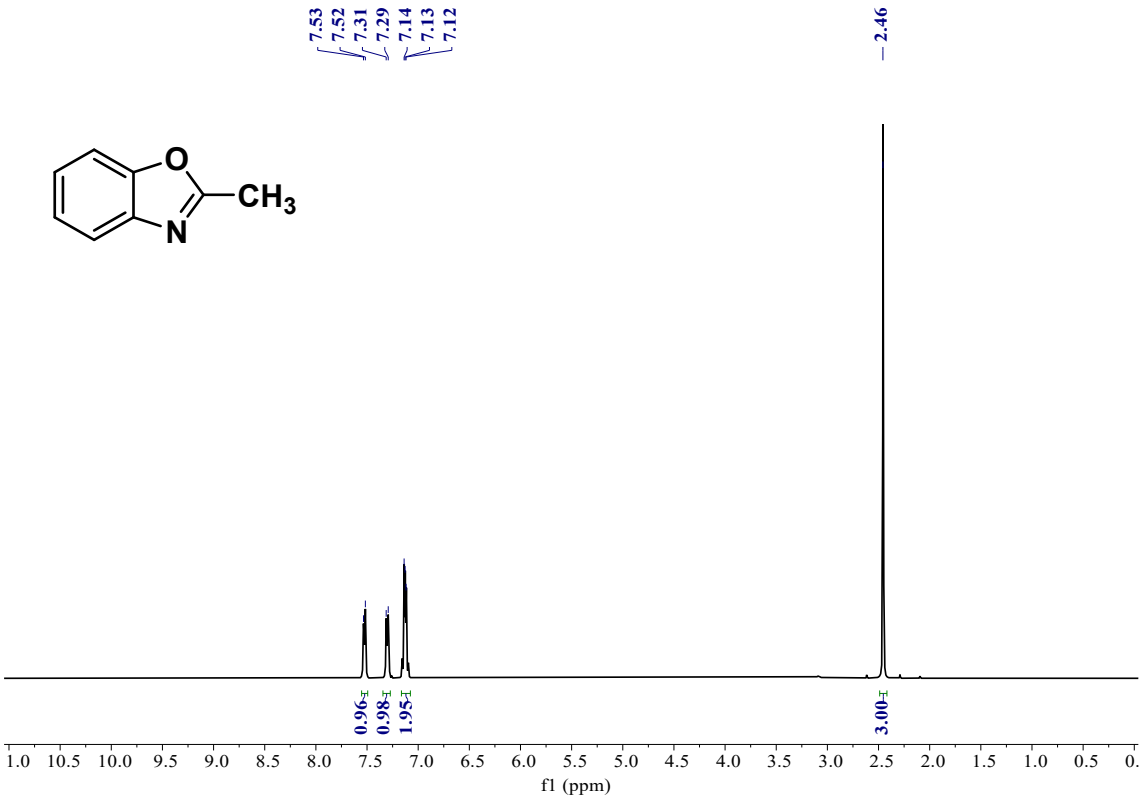
Purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ dichloromethane = 10:1, ethyl acetate as the eluent), 140.37 mg, 67% yield. White soild. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.81-7.73 (m, 1H), 7.60-7.56 (m, 1H), 7.37-7.32 (m, 4H), 2.45 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.5, 152.9, 142.2, 141.8, 129.8, 127.8, 125.1, 124.7, 121.2, 118.8, 110.7, 21.8. **GC-MS** m/z (%): 209.16(100)$[M]^{+\cdot}$, 180.17(14), 91.08(21), 63.07(14).

2-(4-chlorophenyl)benzoxazole(3ae)[10]

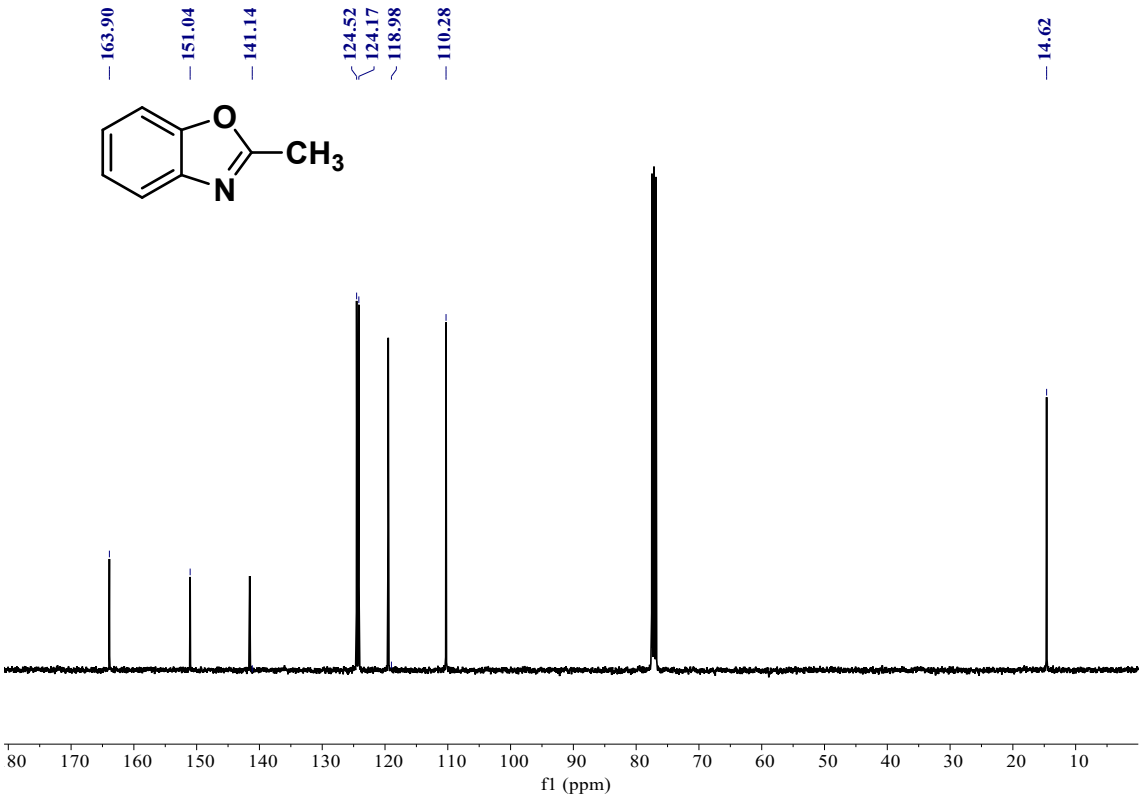


Purified by preparative thin-layer chromatography (PTLC; Petroleum ether/ dichloromethane = 10:1, ethyl acetate as the eluent), 170.28 mg, 82% yield. White soild. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.81-7.73 (m, 1H), 7.54 (dd, *J* = 31.1, 9.0 Hz, 3H), 7.36 (dd, *J* = 6.1, 3.1 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 162.2, 150.9, 142.1, 137.9, 129.4, 129.0, 125.8, 125.5, 124.9, 120.2, 110.8. **GC-MS** m/z (%): 229.08(100)$[M]^{+\cdot}$, 231.06(33)$[M+2]^{+\cdot}$,201.0(15), 166.10(12), 92.05(21), 63.06(22).

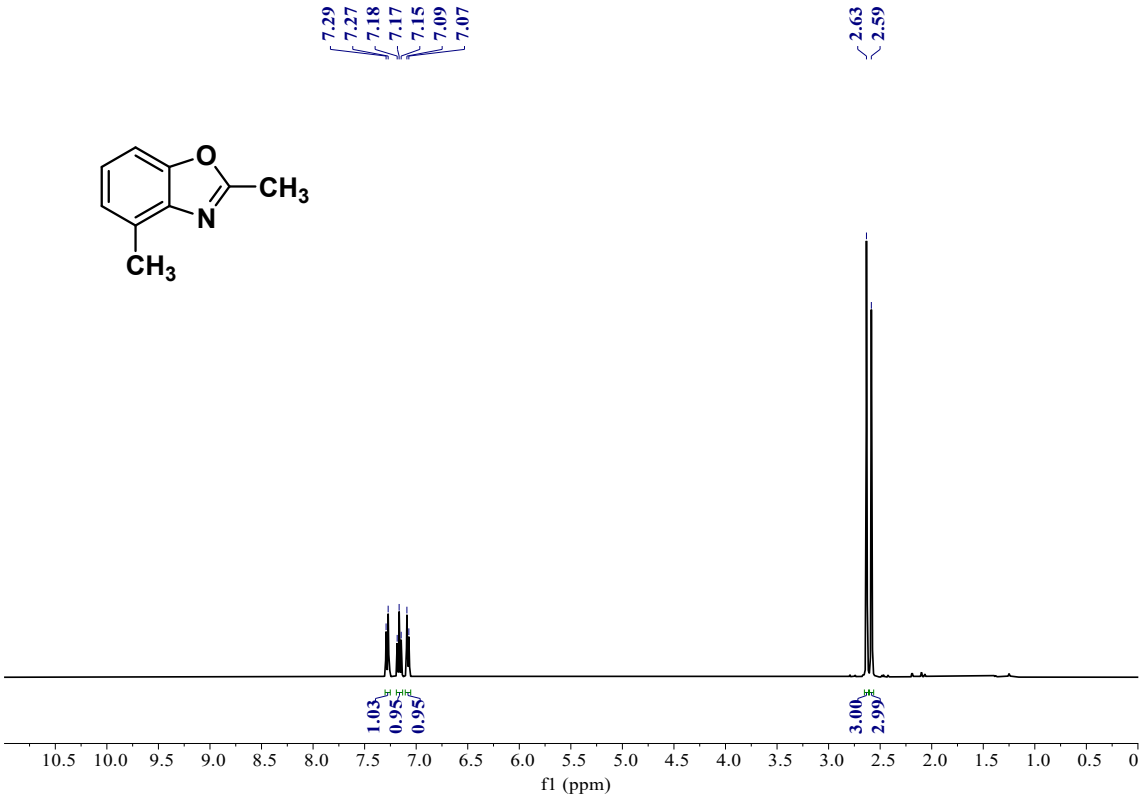
9. NMR spectra



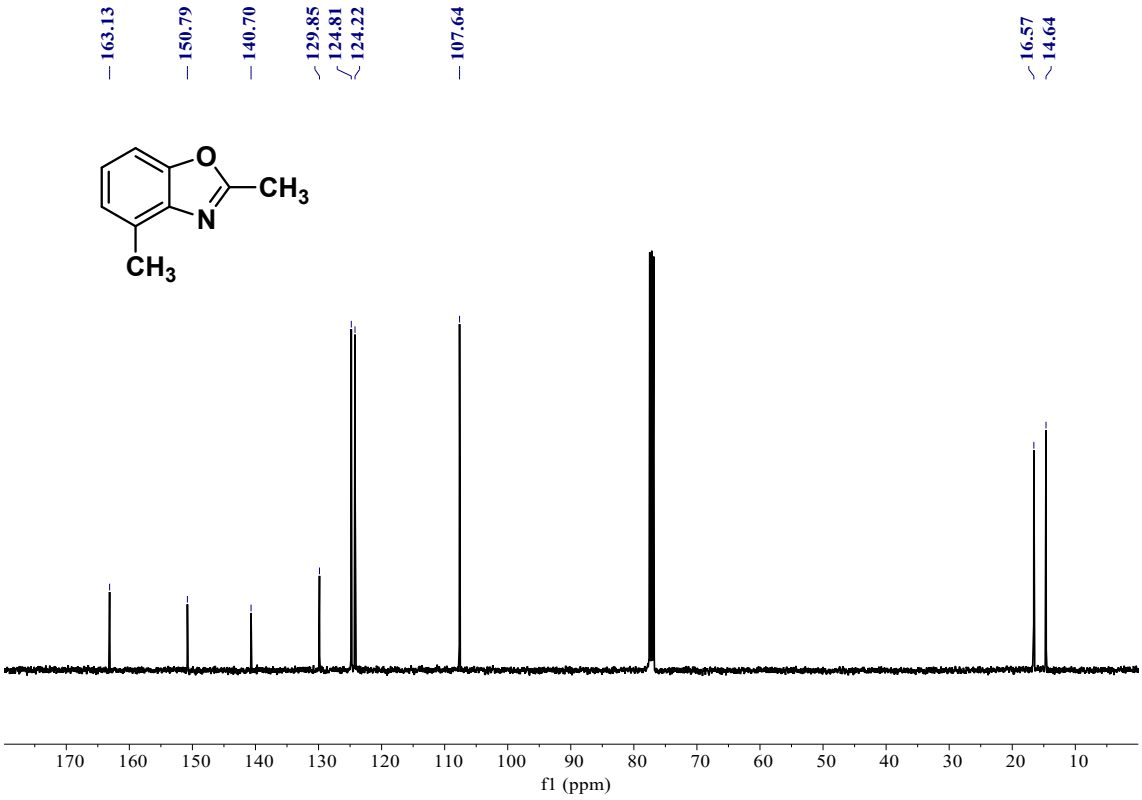
^{1}H NMR for product 3a (400 MHz, $CDCl_3$)



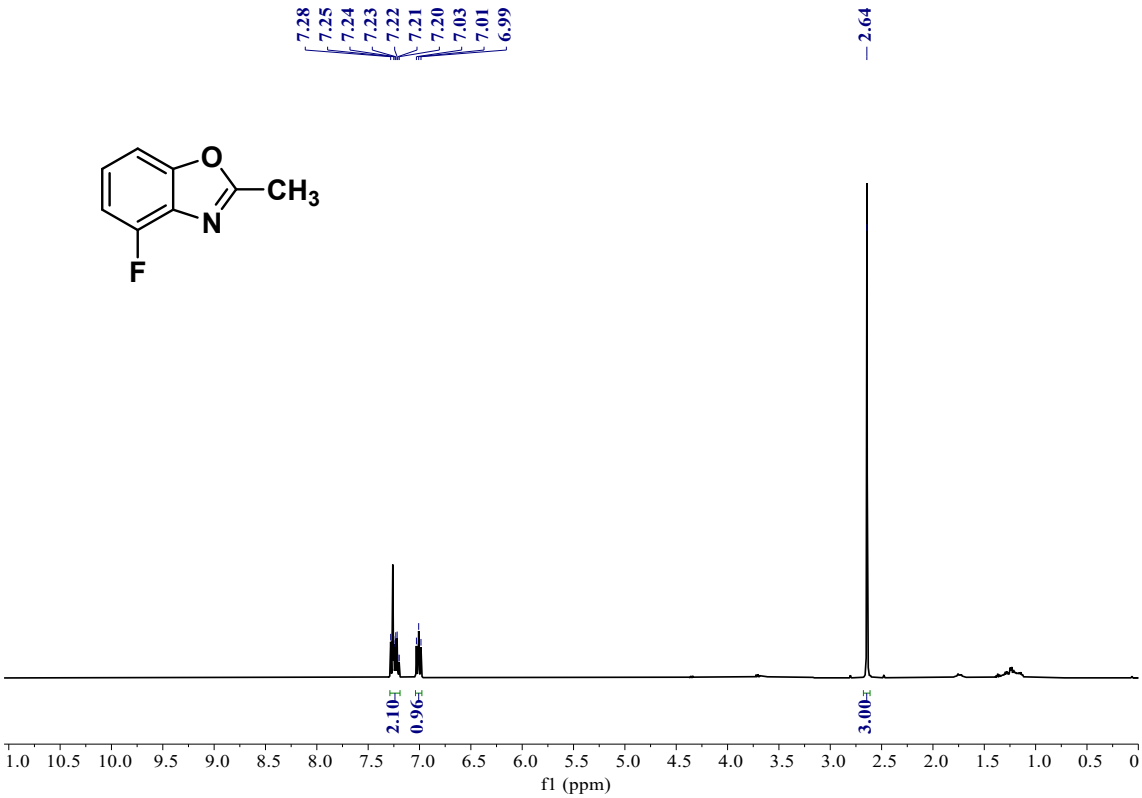
^{13}C NMR for product 3a (101 MHz, $CDCl_3$)



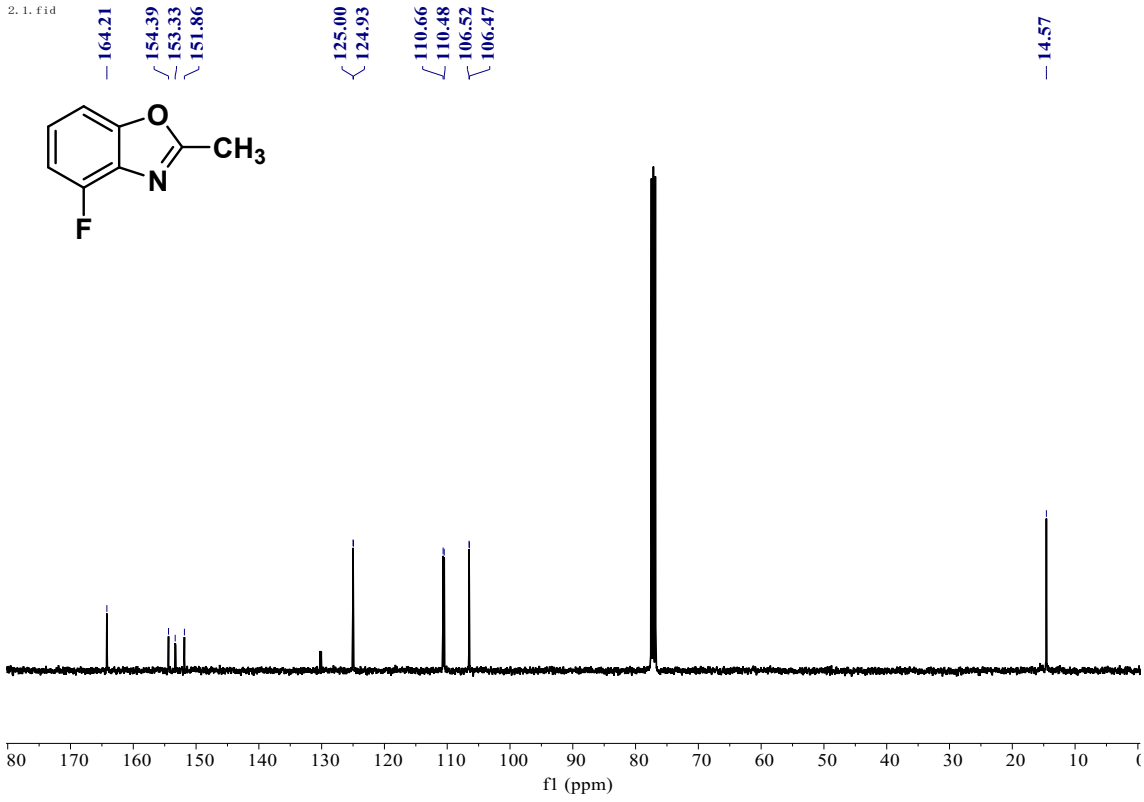
^{1}H NMR for product 3b (400 MHz, $CDCl_3$)



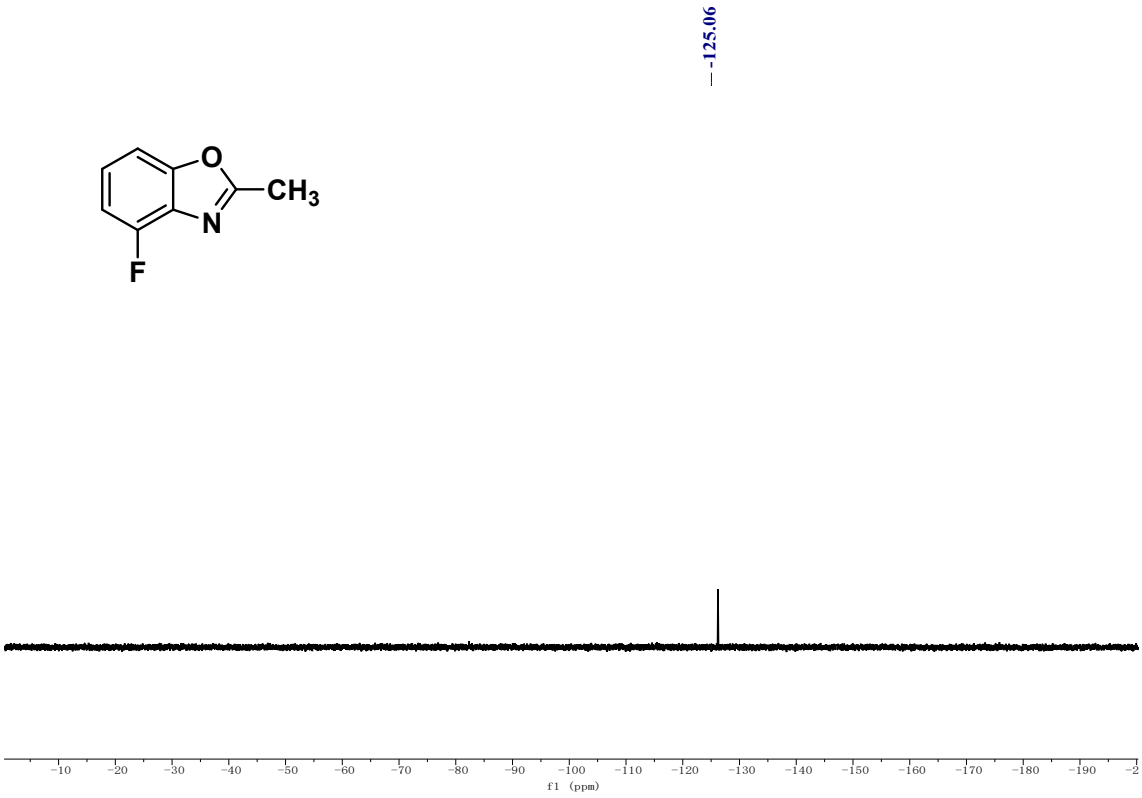
^{13}C NMR for product 3b (101 MHz, $CDCl_3$)



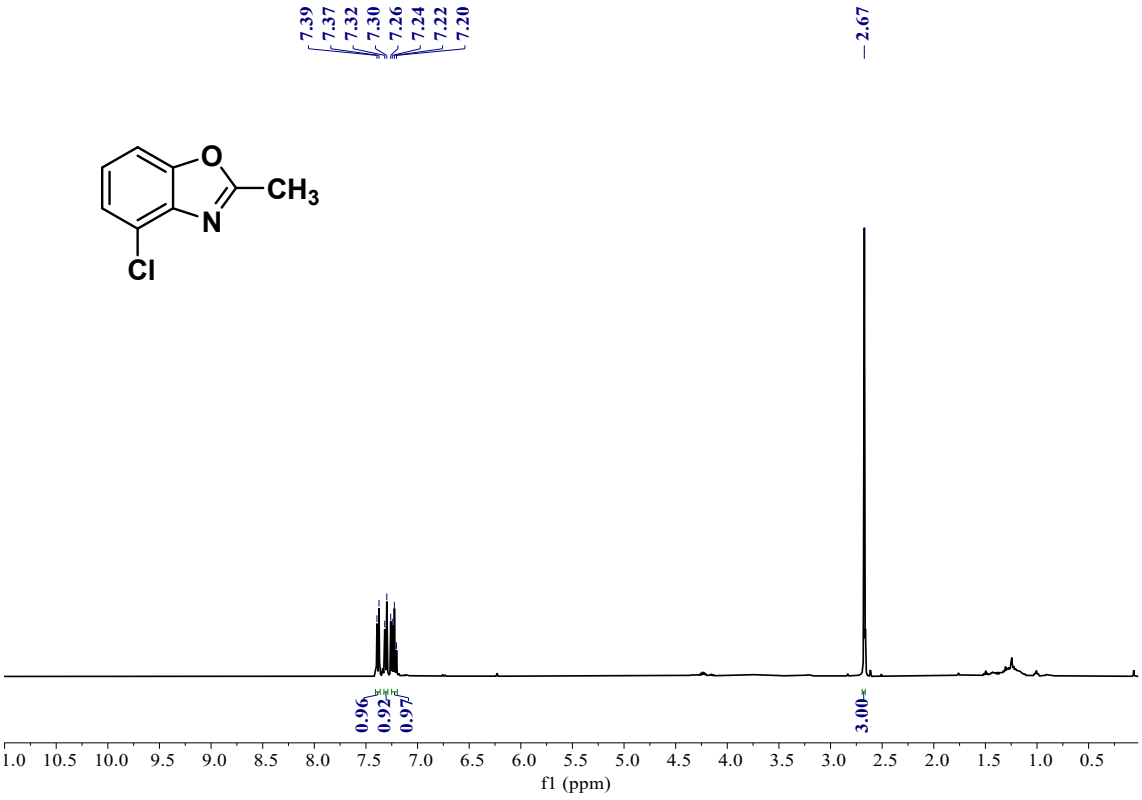
^{1}H NMR for product 3c (400 MHz, $CDCl_3$)



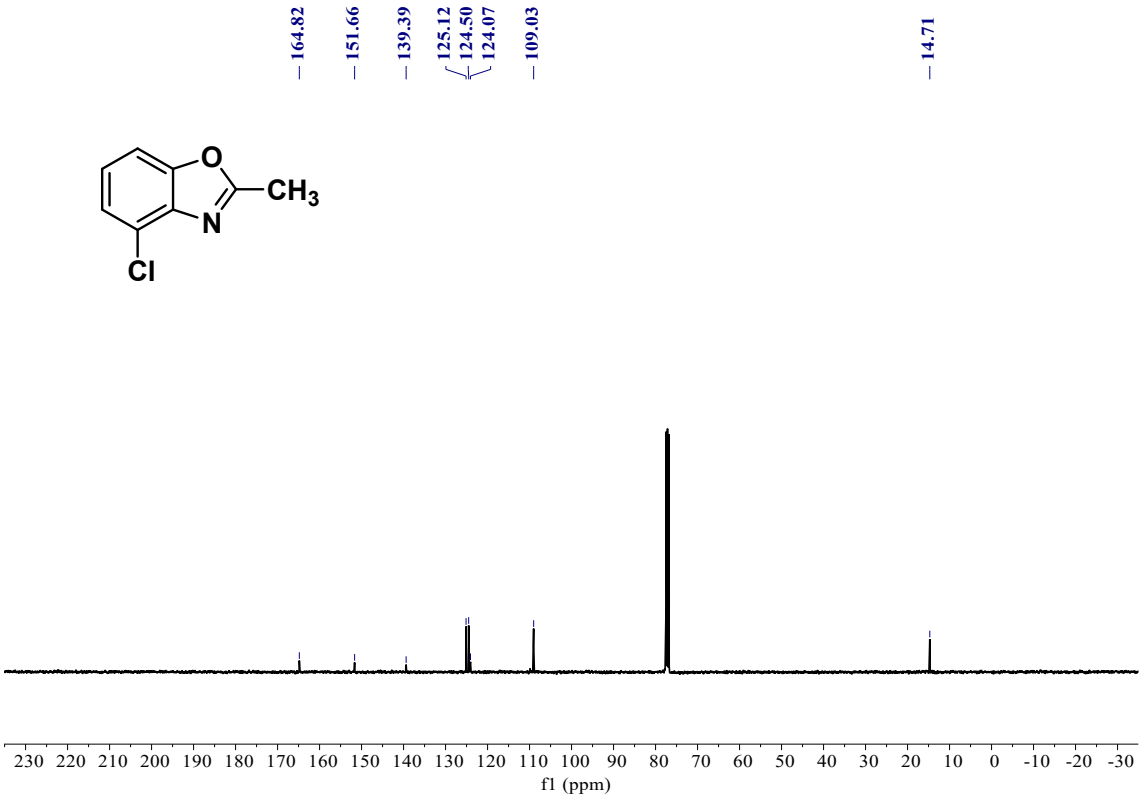
^{13}C NMR for product 3c (101 MHz, $CDCl_3$)



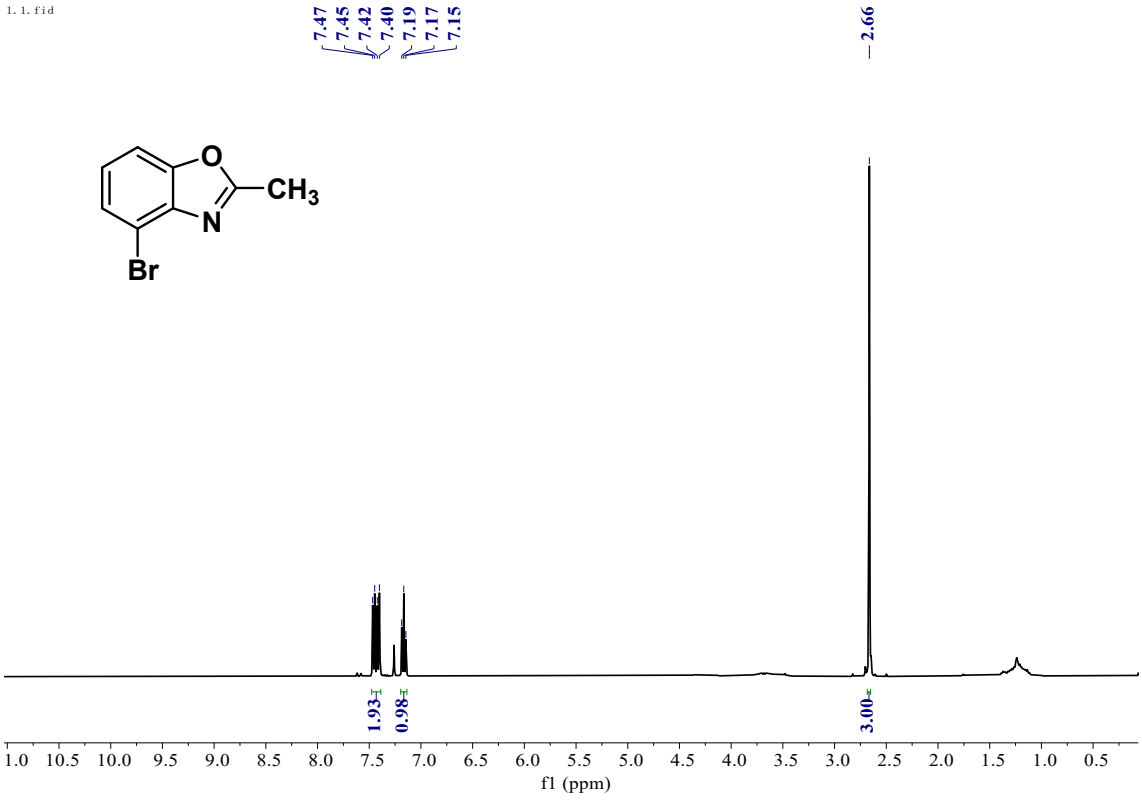
^{19}F NMR for product 3c (470 MHz, $CDCl_3$)



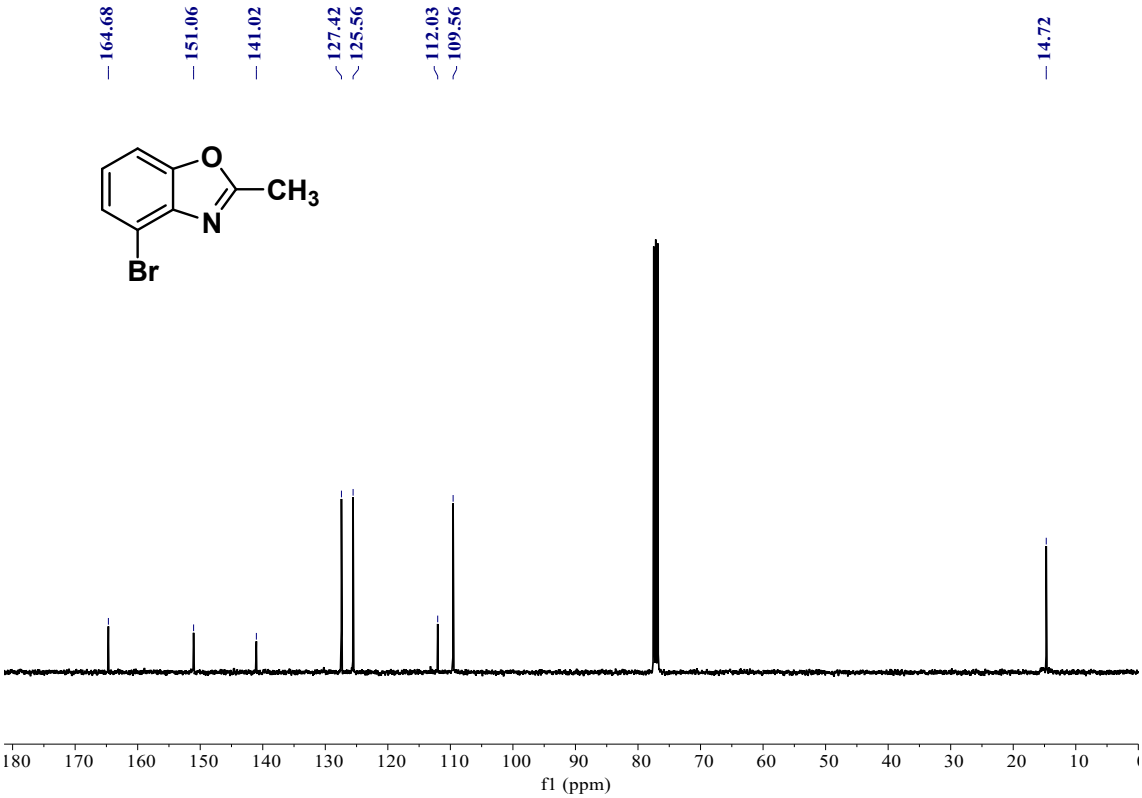
^{1}H NMR for product 3d (400 MHz, $CDCl_3$)



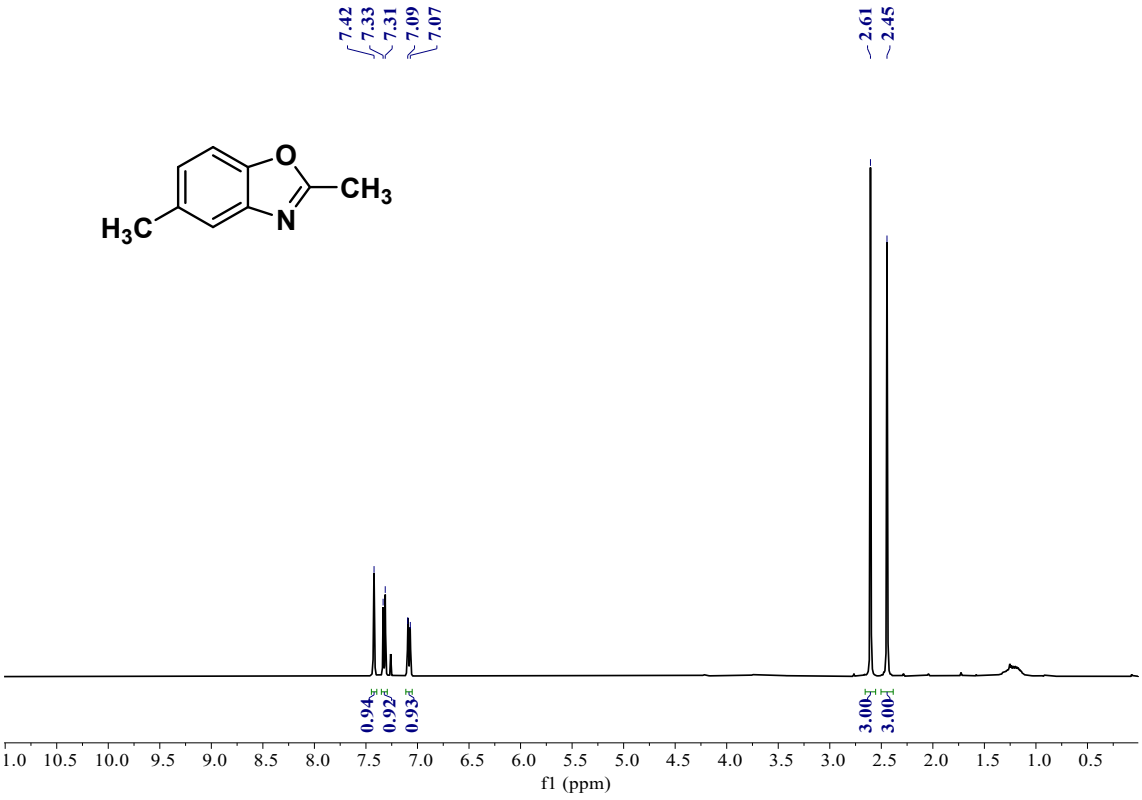
^{13}C NMR for product 3d (101 MHz, $CDCl_3$)



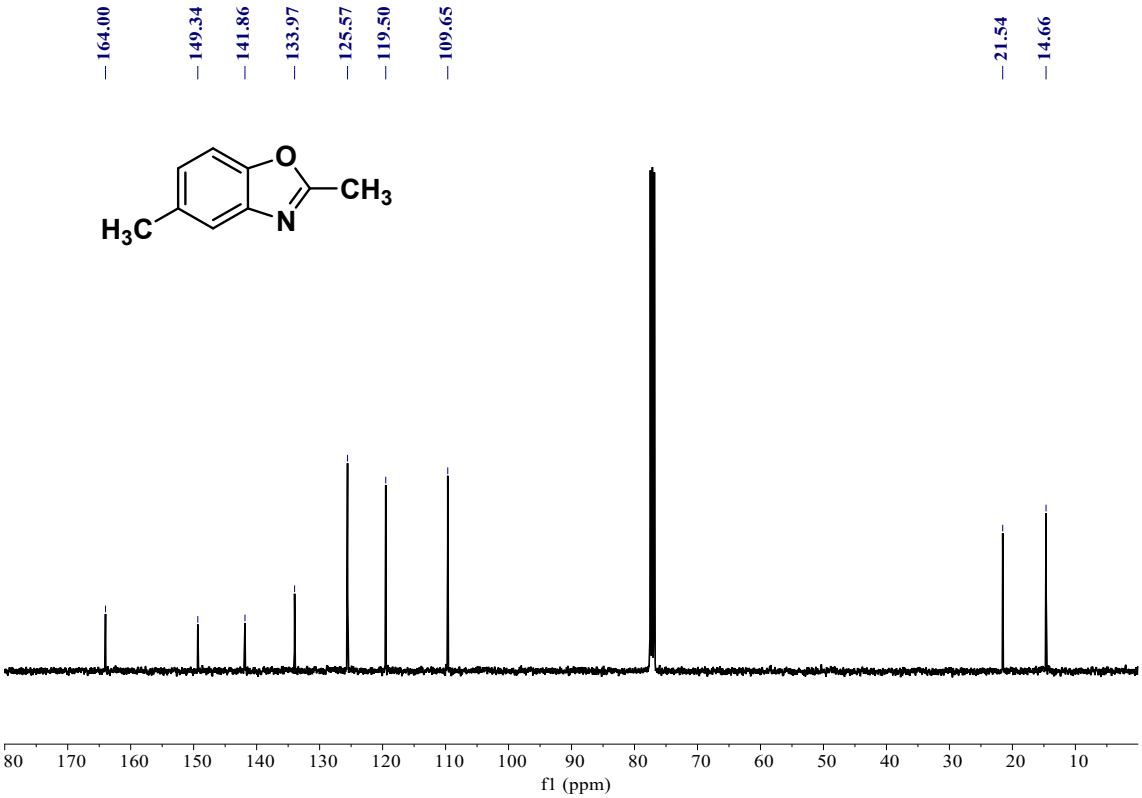
^{1}H NMR for product 3e (400 MHz, $CDCl_3$)



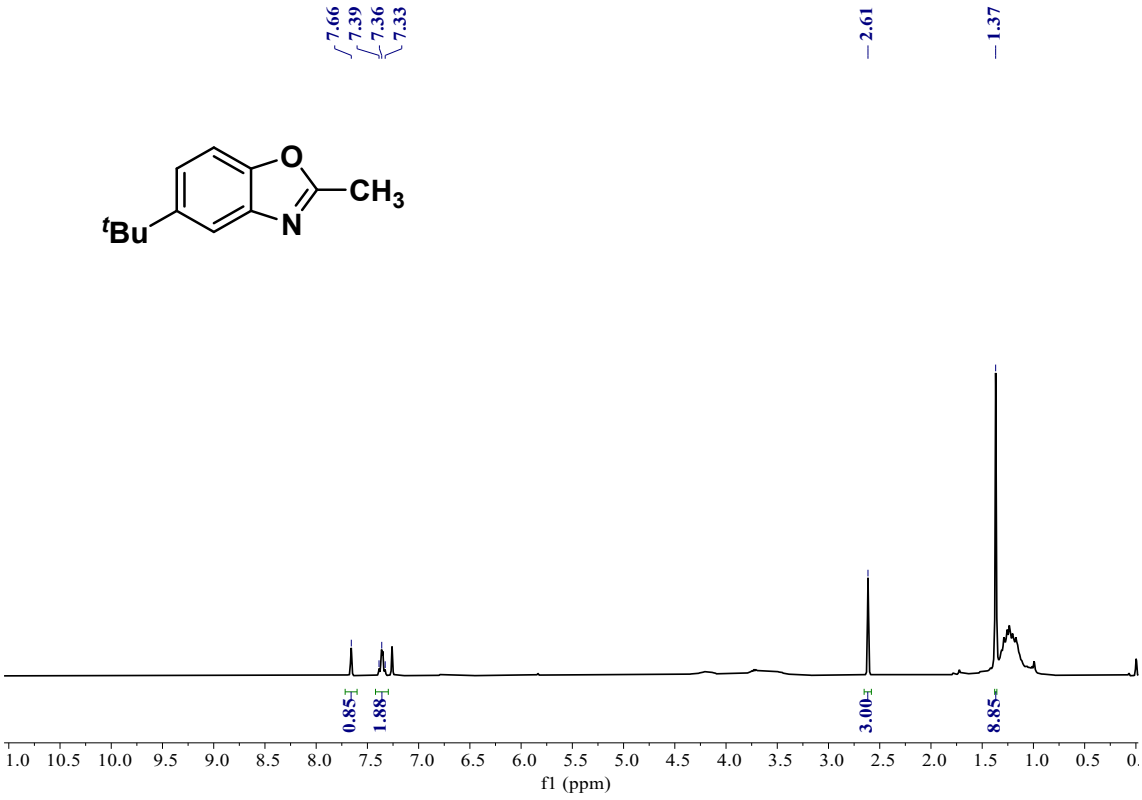
^{13}C NMR for product 3e (101 MHz, $CDCl_3$)



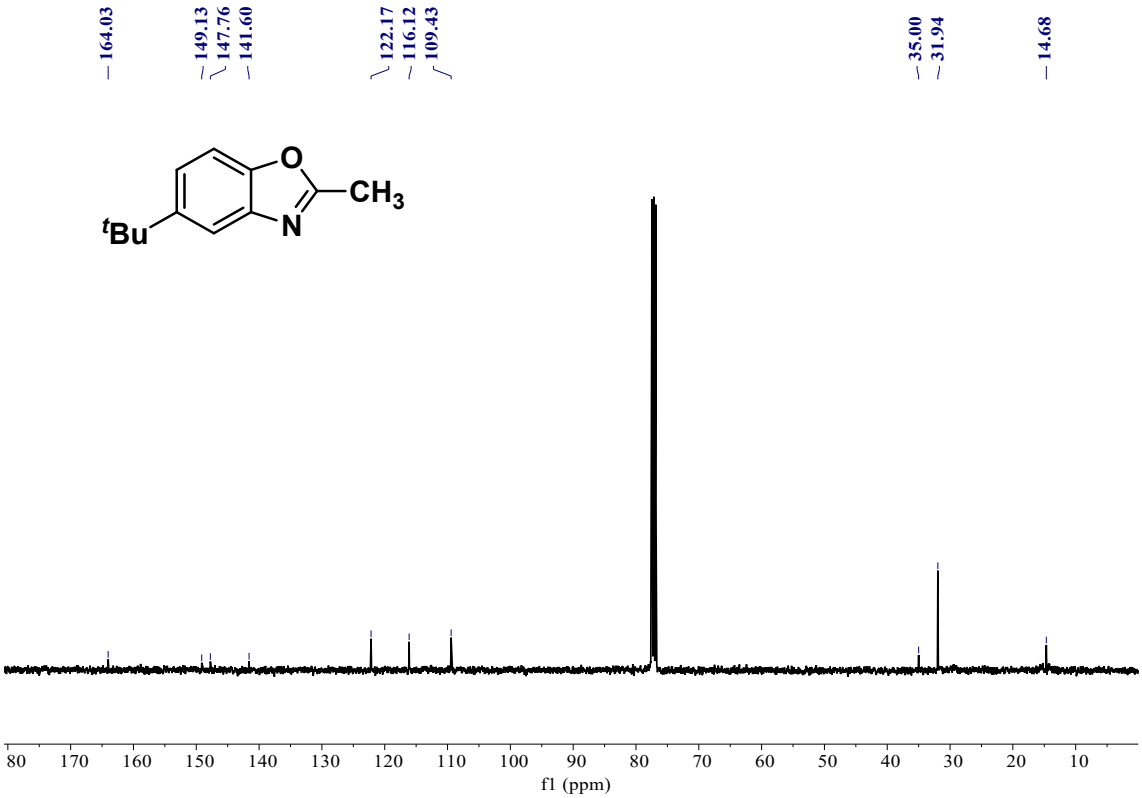
^{1}H NMR for product 3f (400 MHz, $CDCl_3$)



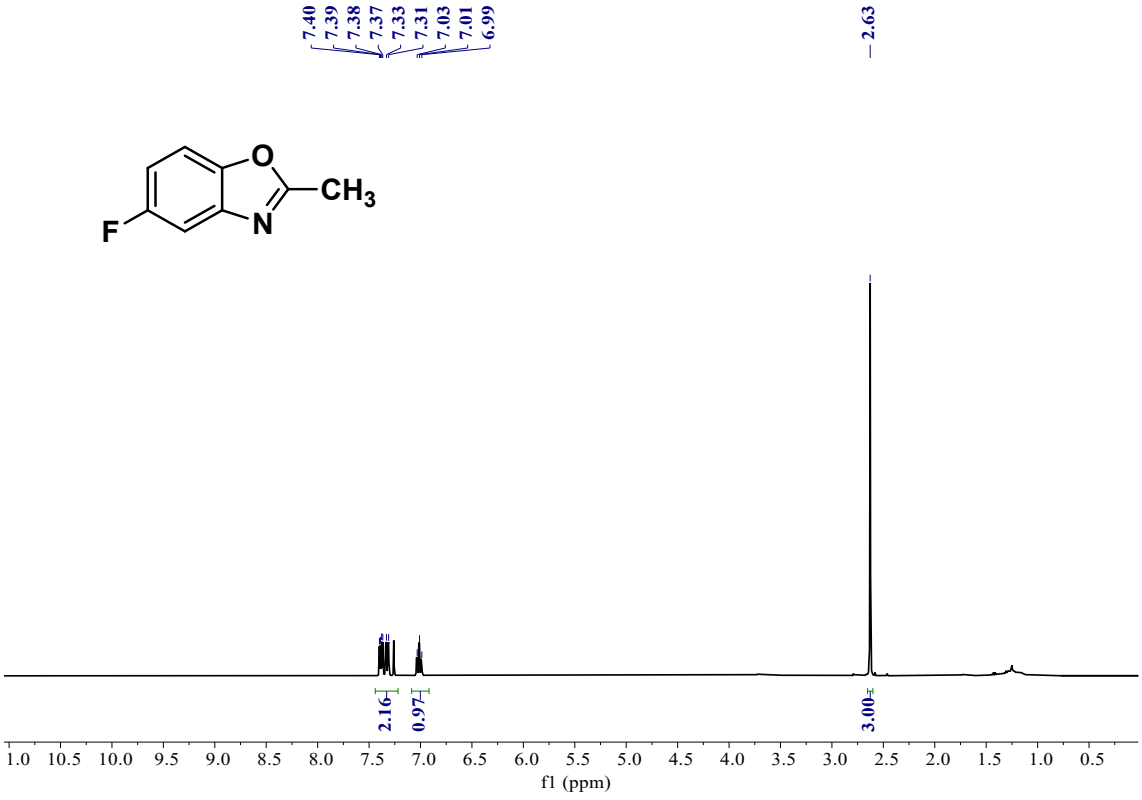
^{13}C NMR for product 3f (101 MHz, $CDCl_3$)



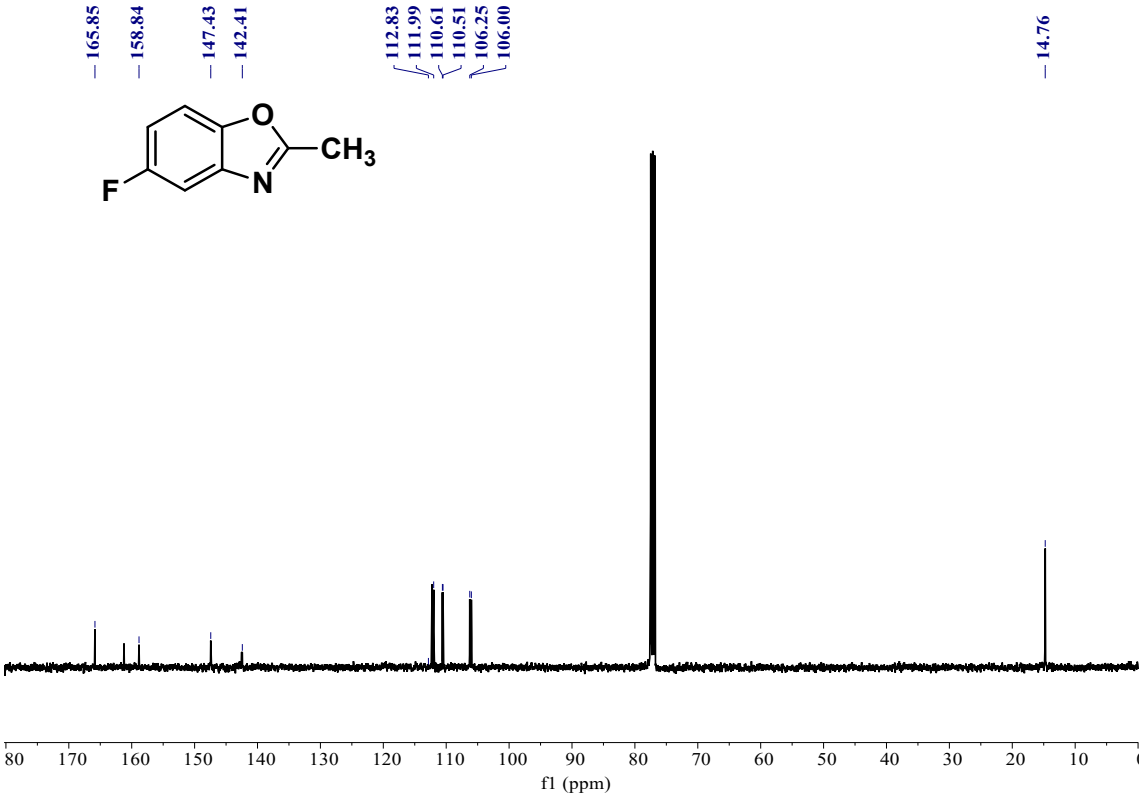
^{1}H NMR for product 3g (400 MHz, $CDCl_3$)



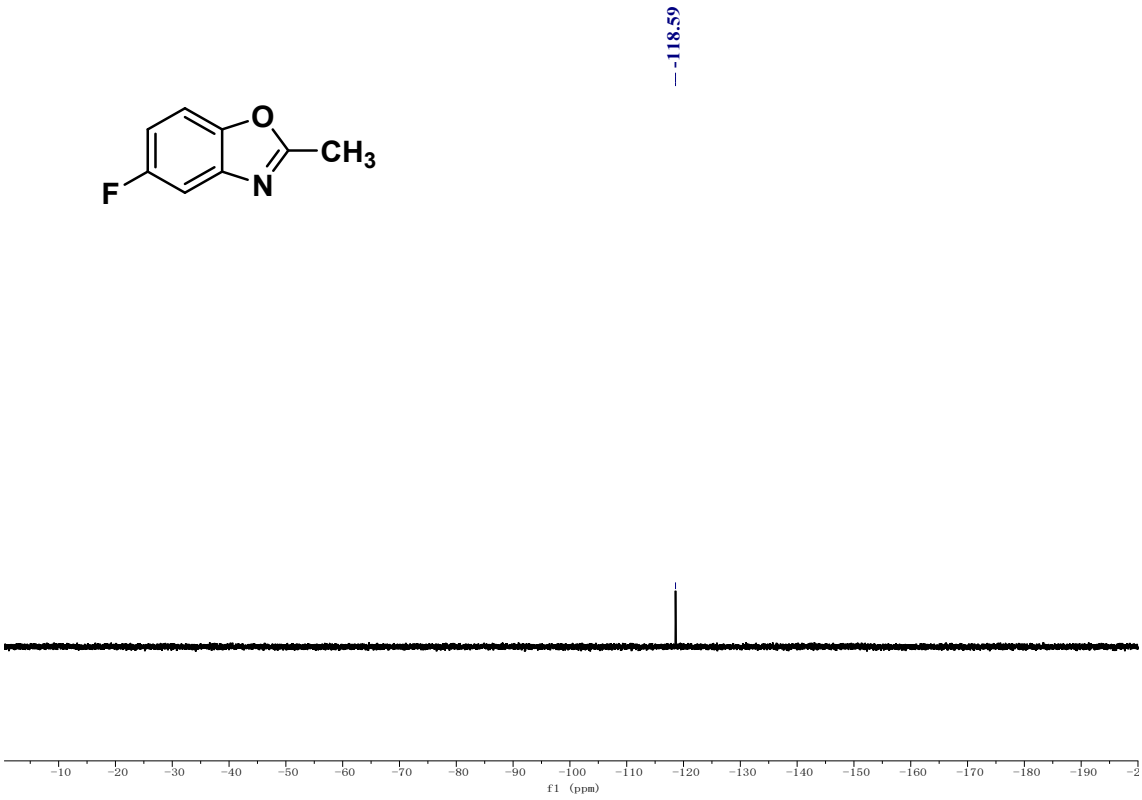
^{13}C NMR for product 3g (101 MHz, $CDCl_3$)



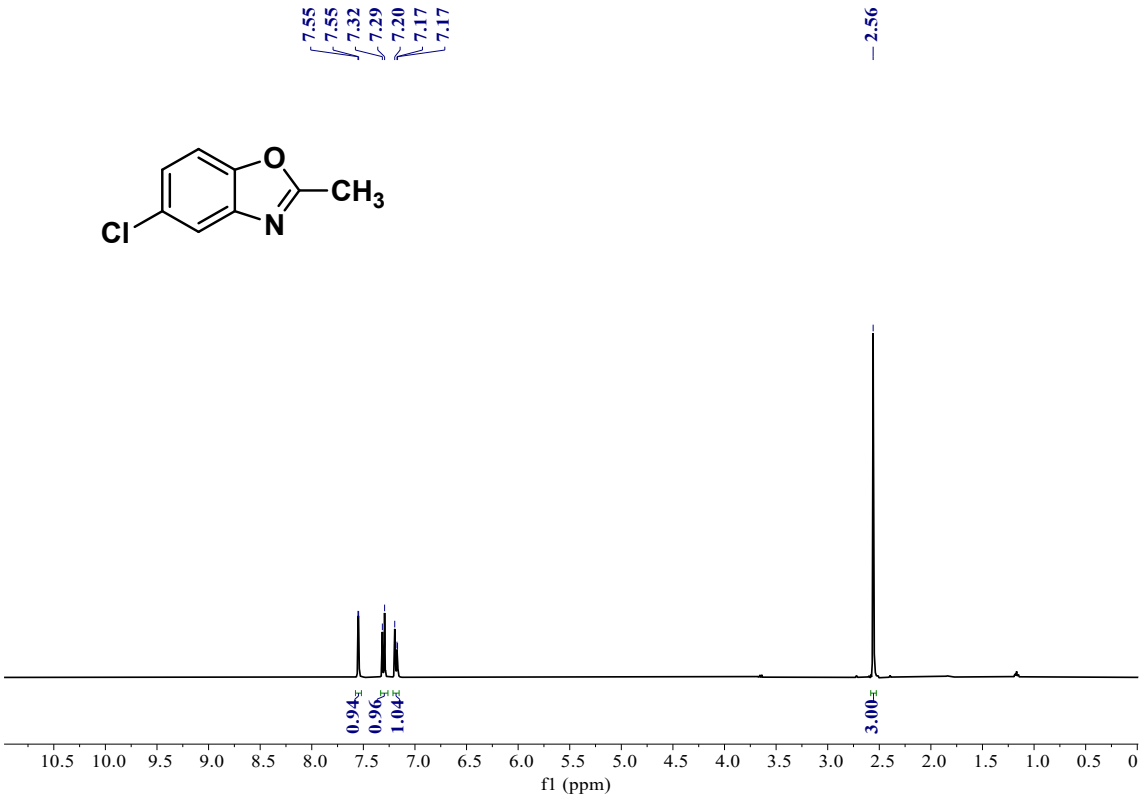
^{1}H NMR for product 3h (400 MHz, $CDCl_3$)



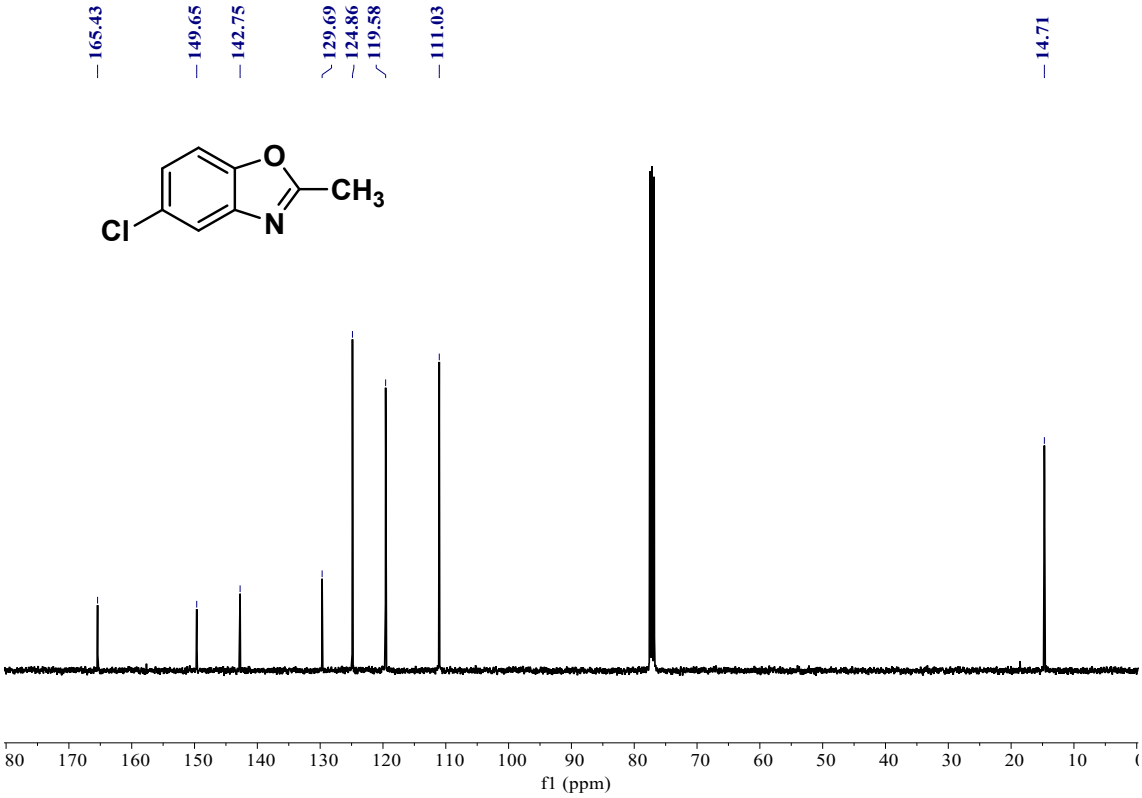
^{13}C NMR for product 3h (101 MHz, $CDCl_3$)



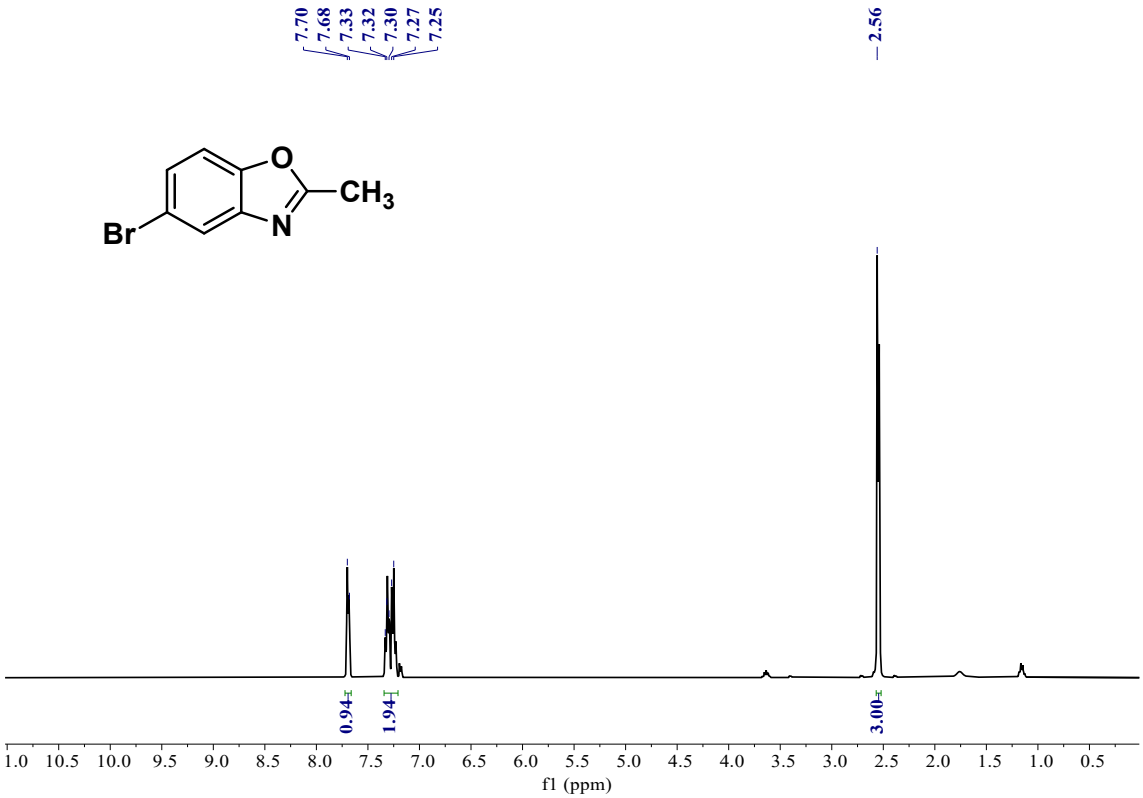
^{19}F NMR for product 3h (470 MHz, $CDCl_3$)



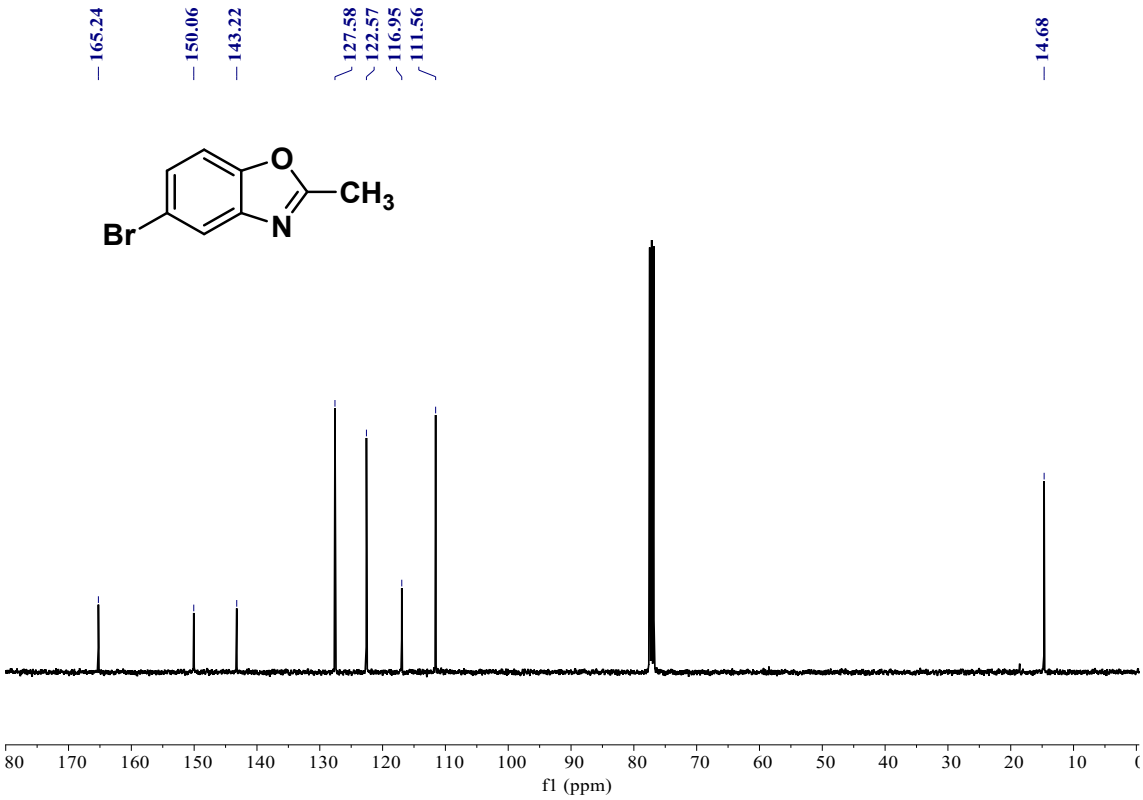
^{1}H NMR for product 3i (400 MHz, $CDCl_3$)



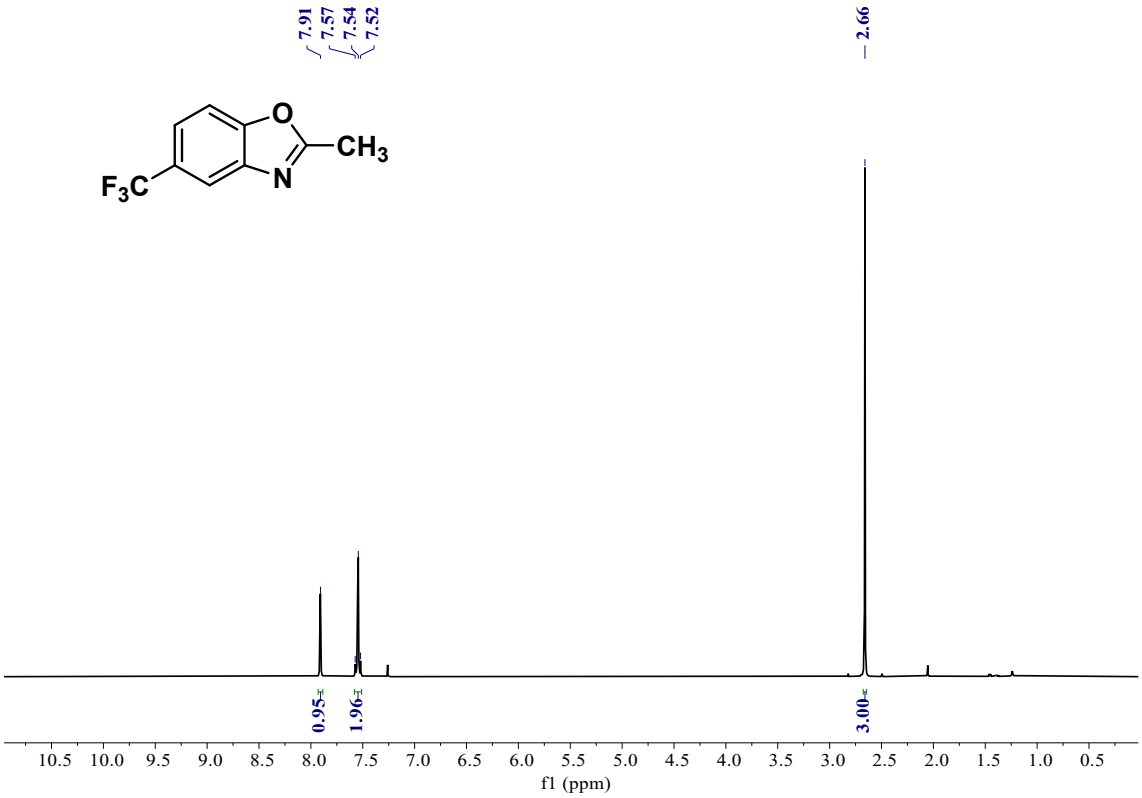
^{13}C NMR for product 3i (101 MHz, $CDCl_3$)



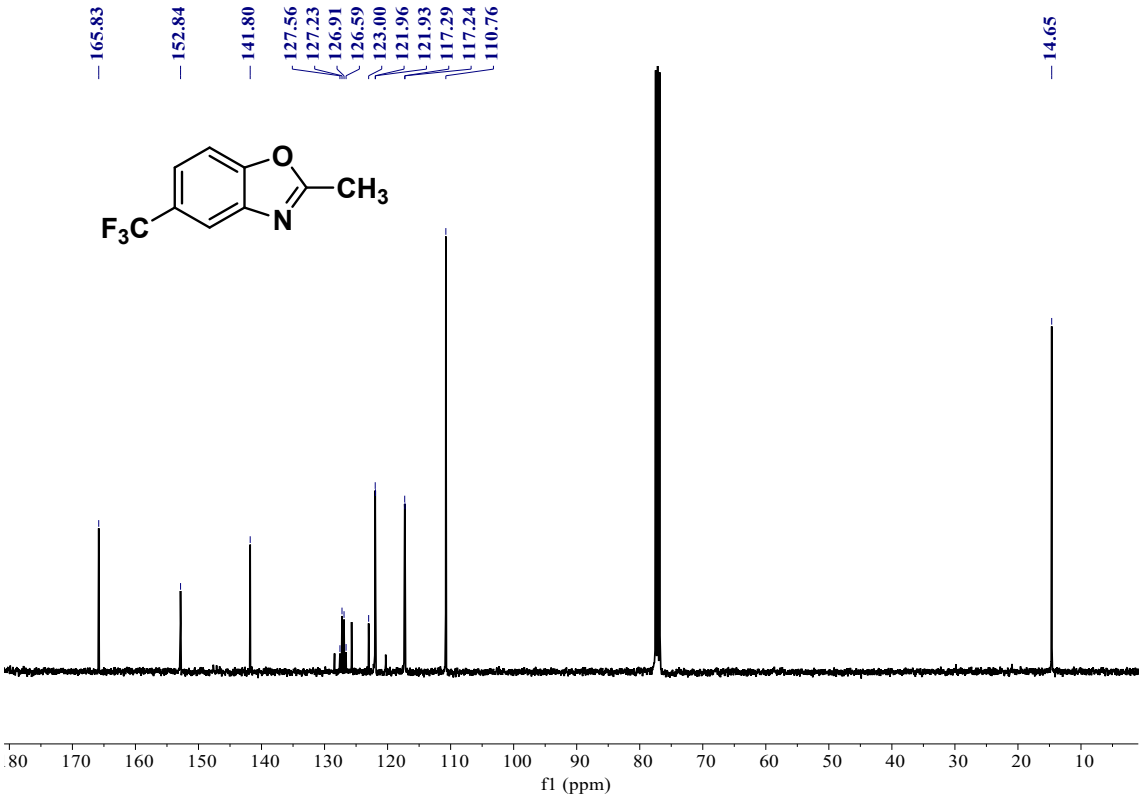
^{1}H NMR for product 3j (400 MHz, $CDCl_3$)



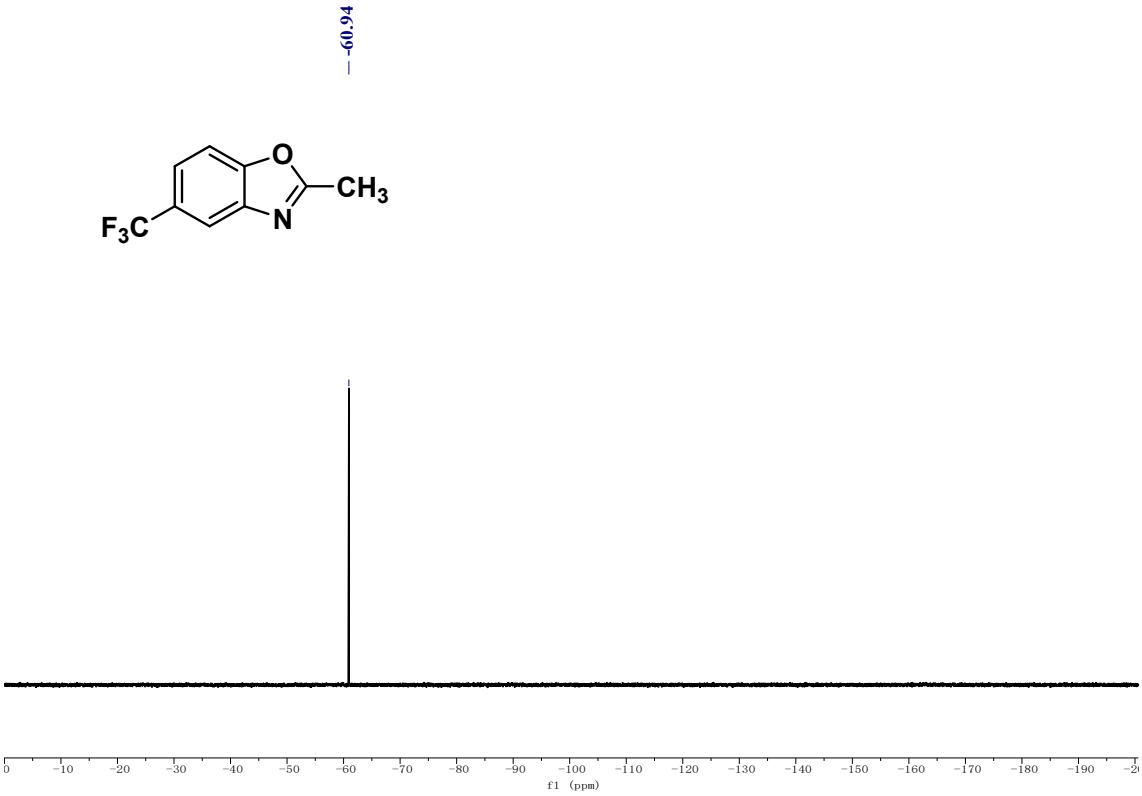
^{13}C NMR for product 3j (101 MHz, $CDCl_3$)



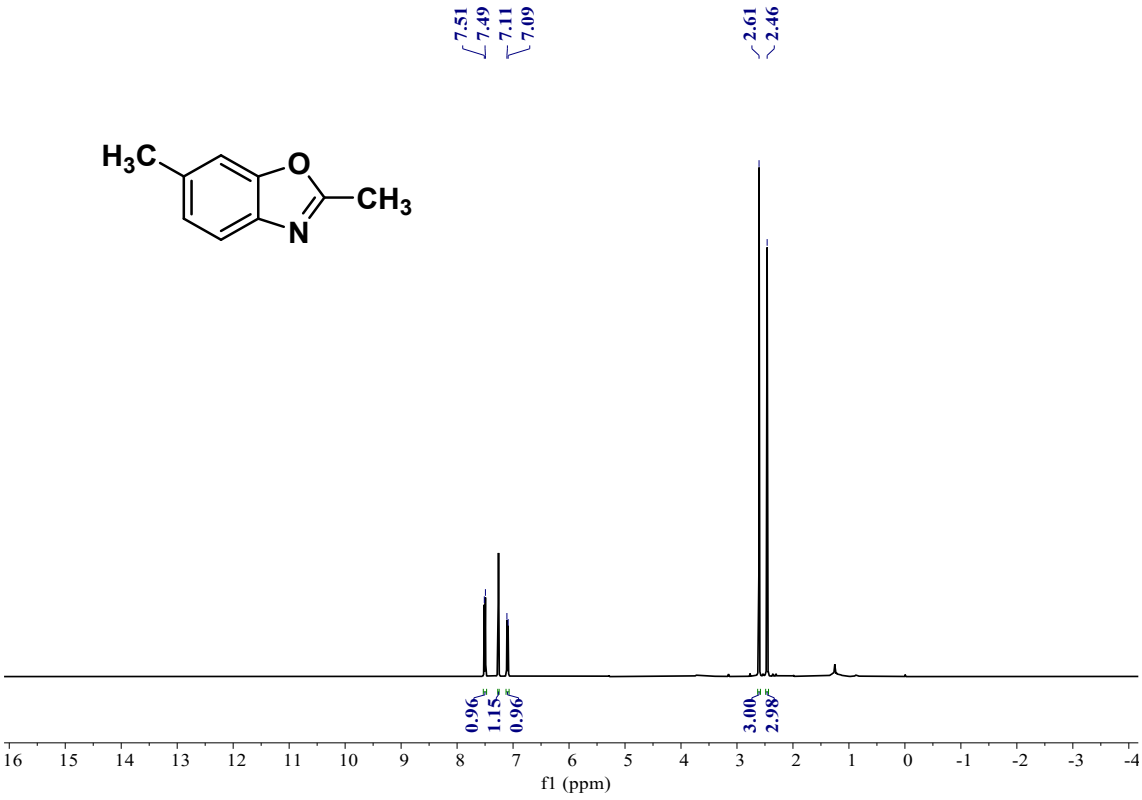
^{1}H NMR for product 3k (400 MHz, $CDCl_3$)



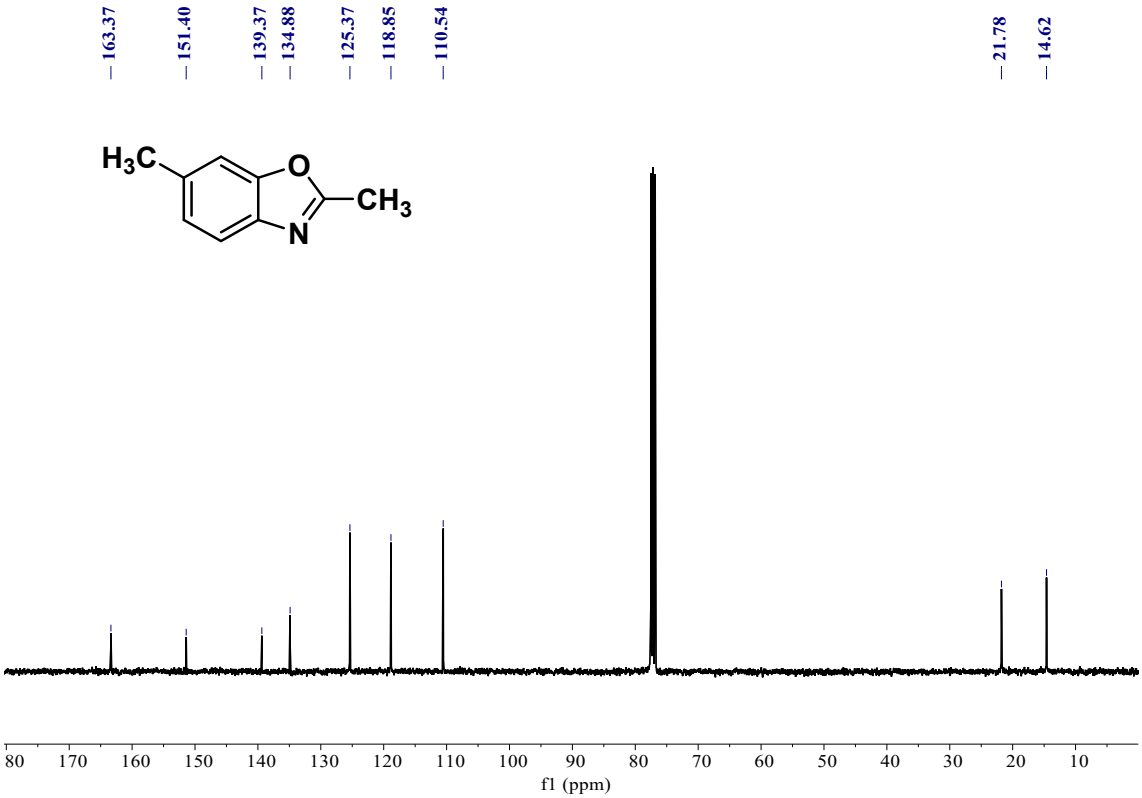
^{13}C NMR for product 3k (101 MHz, $CDCl_3$)



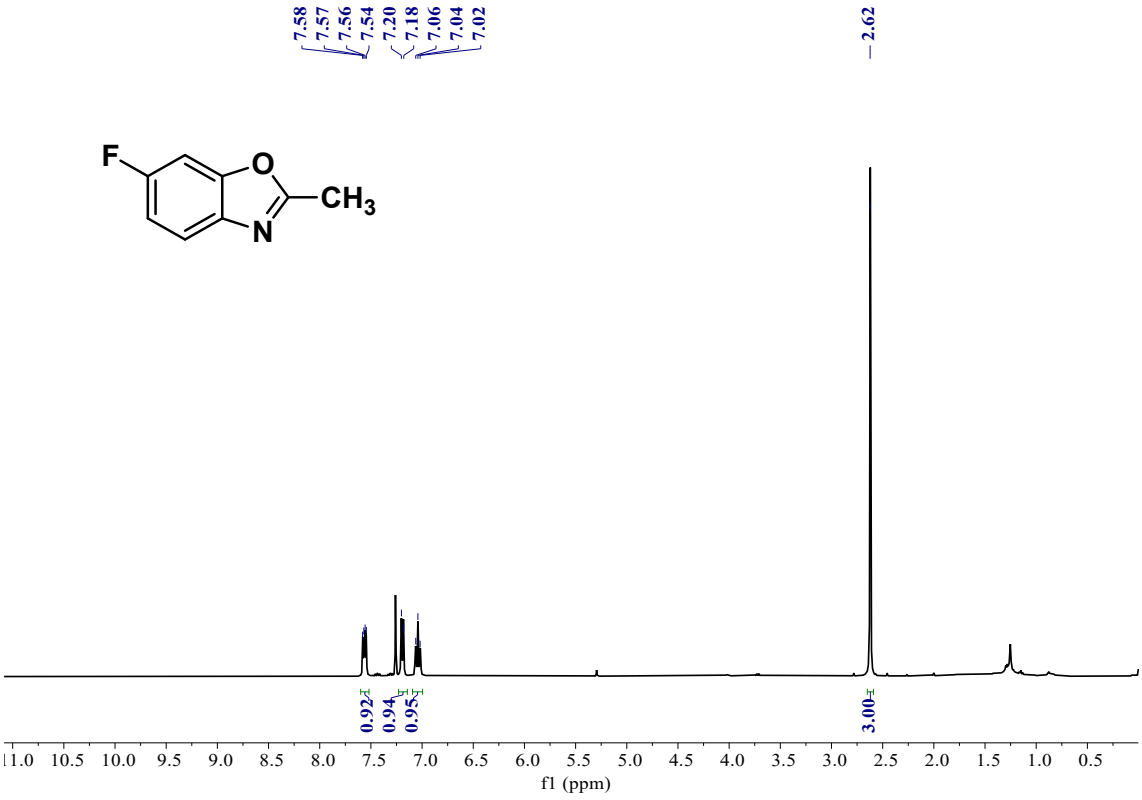
^{19}F NMR for product 3k (470 MHz, $CDCl_3$)



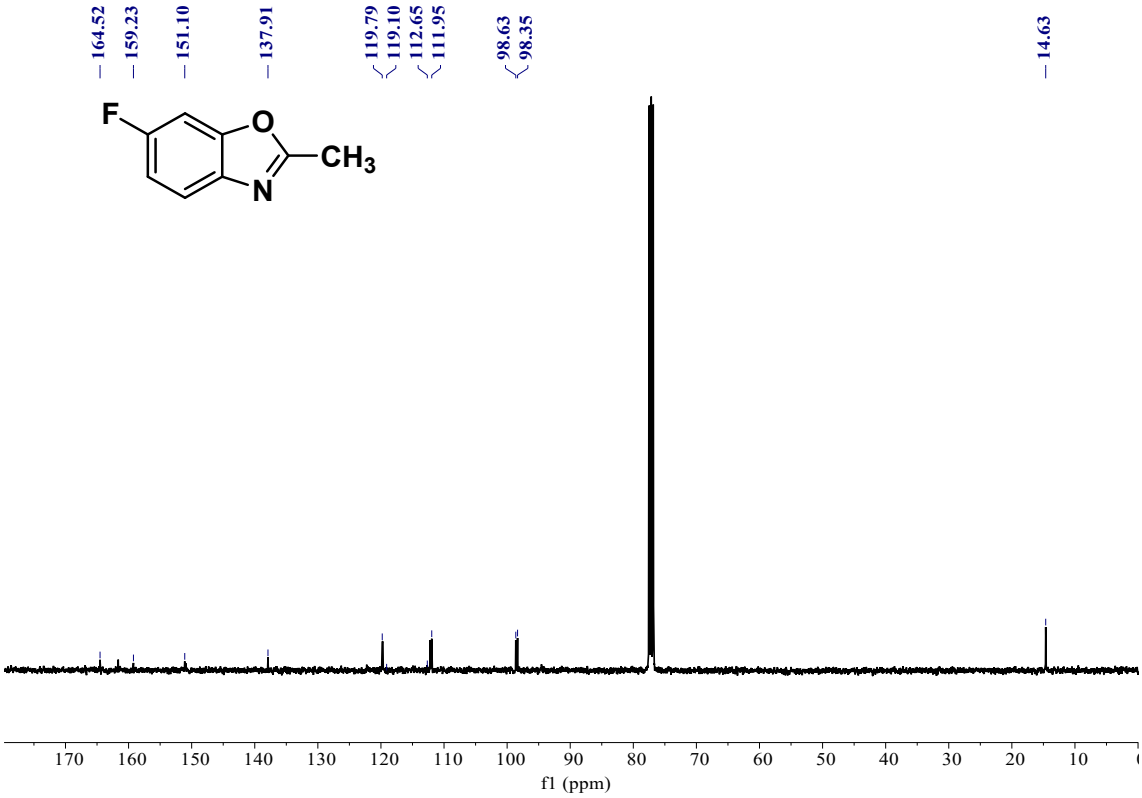
^{1}H NMR for product 3l (400 MHz, $CDCl_3$)



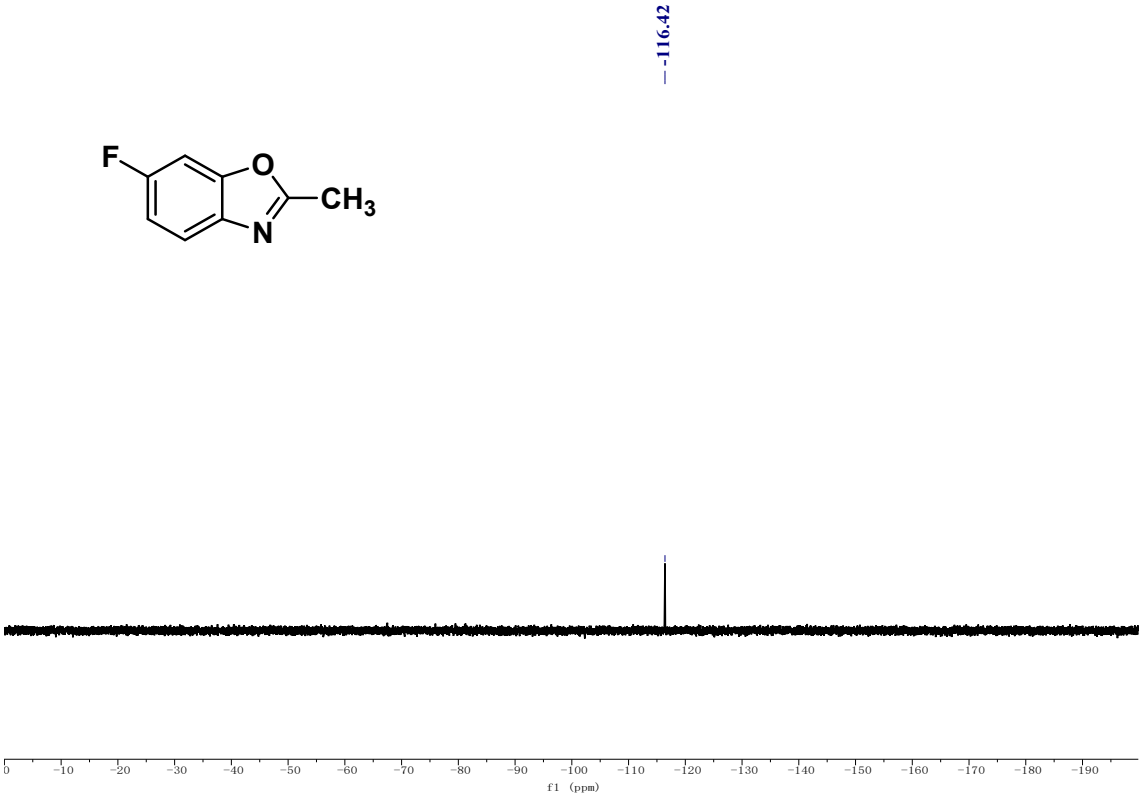
^{13}C NMR for product 3l (101 MHz, $CDCl_3$)



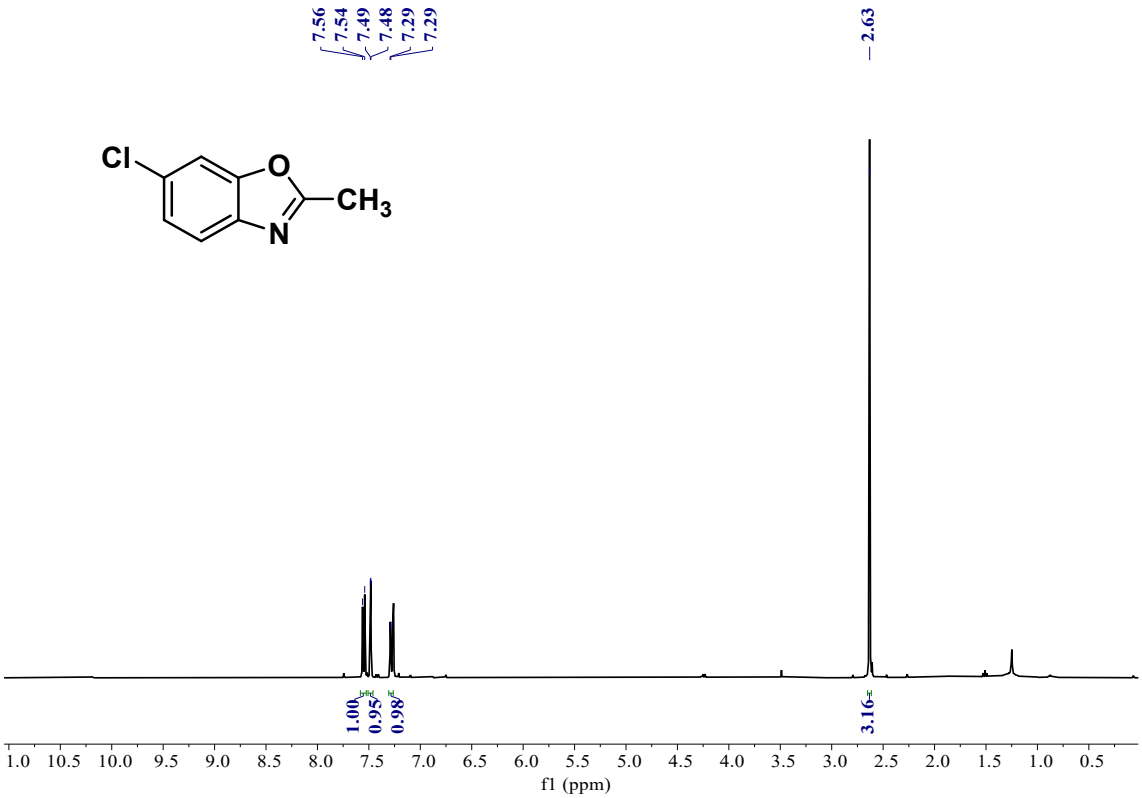
^{1}H NMR for product 3m (400 MHz, $CDCl_3$)



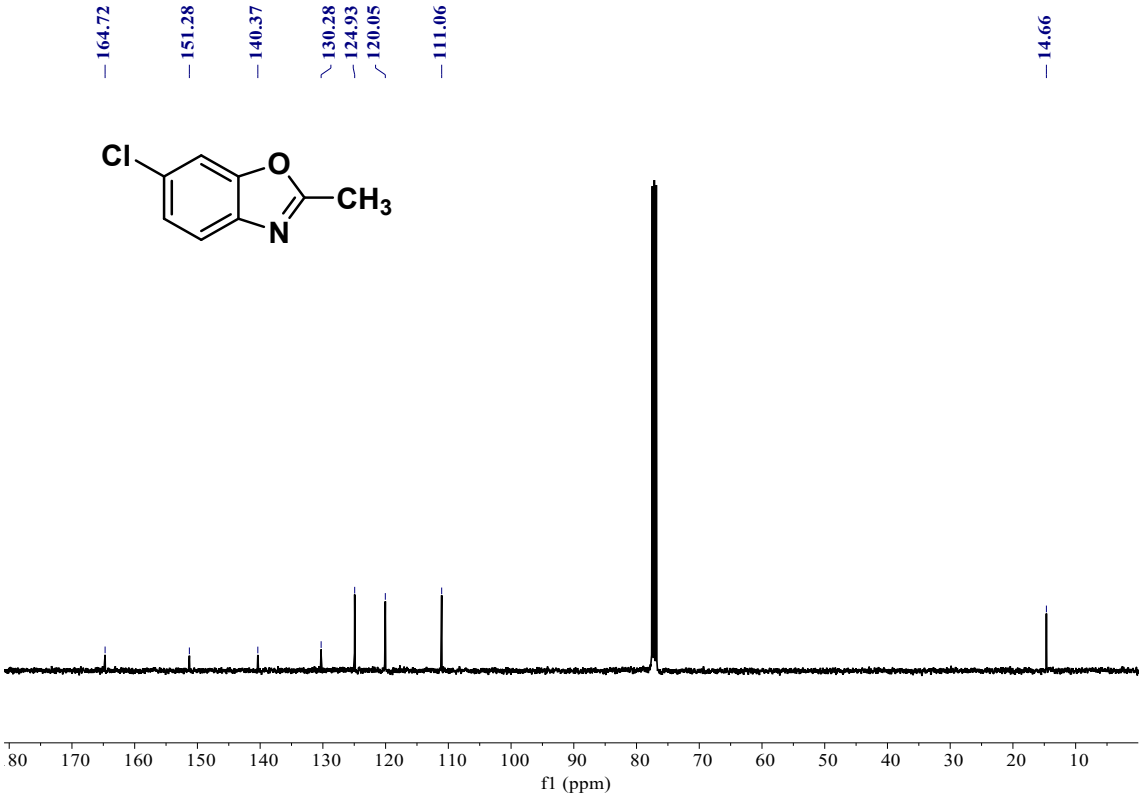
^{13}C NMR for product 3m (101 MHz, $CDCl_3$)



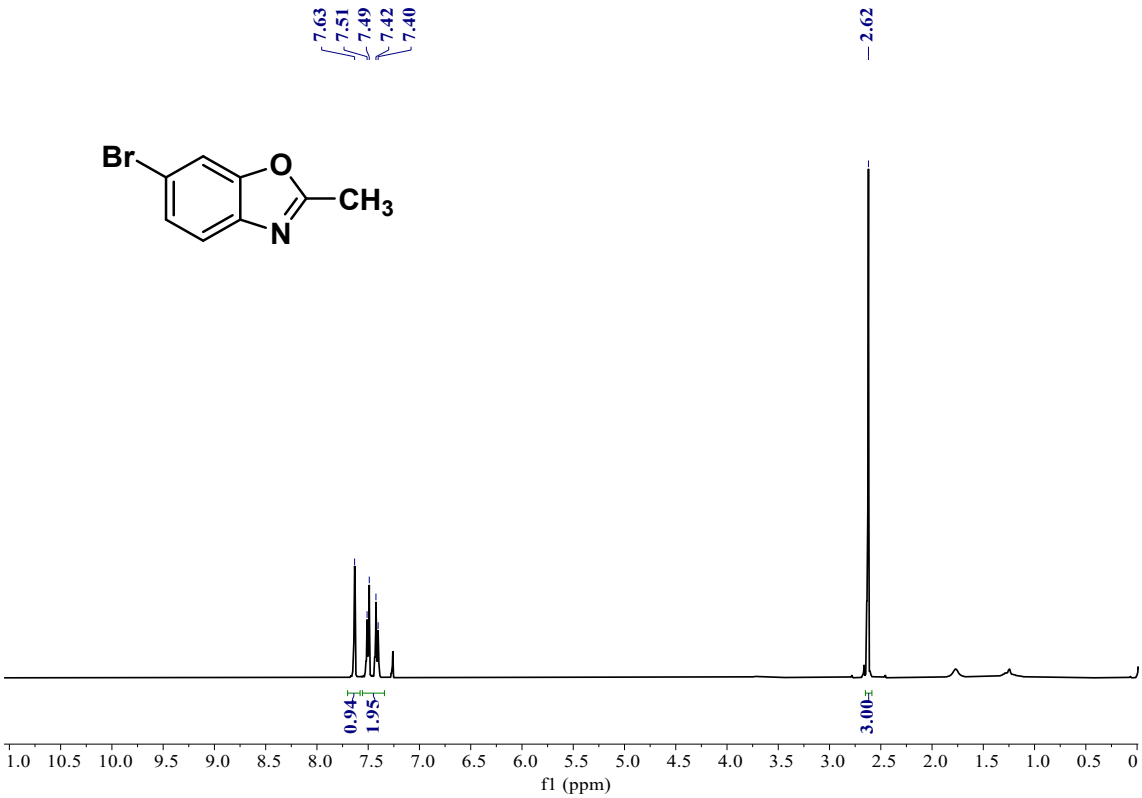
^{19}F NMR for product 3m (470 MHz, $CDCl_3$)



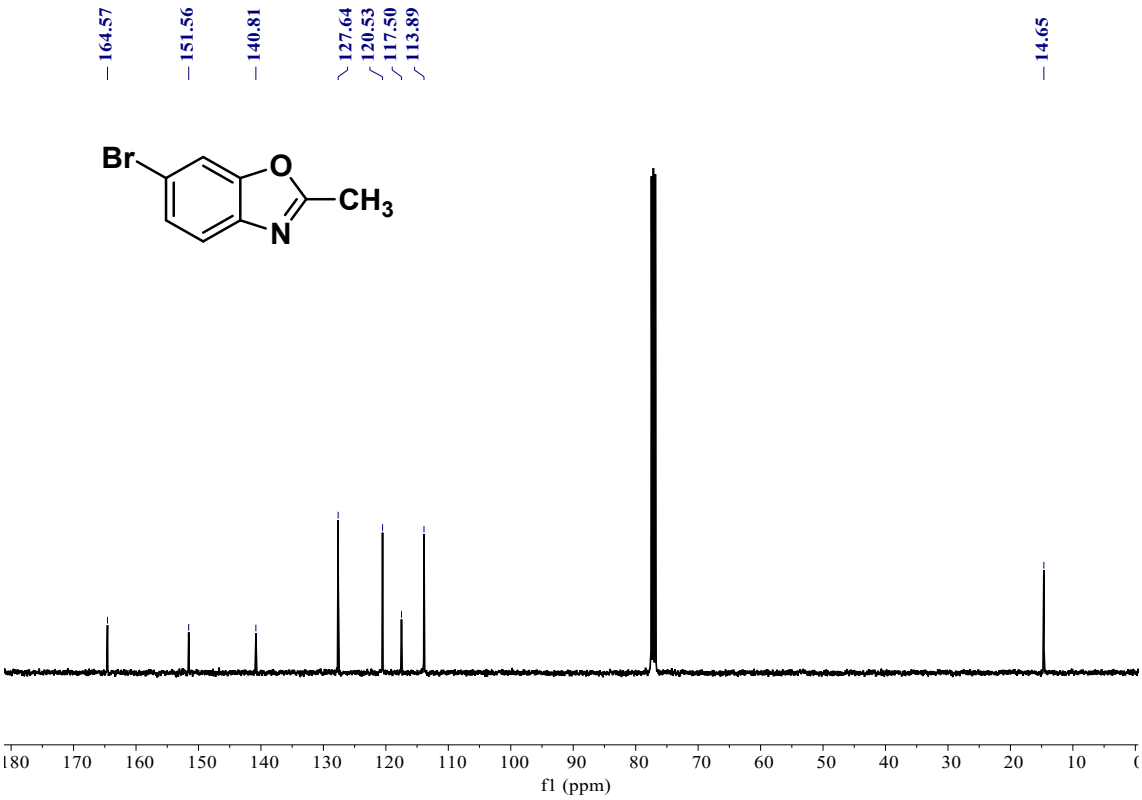
^{1}H NMR for product 3n (400 MHz, $CDCl_3$)



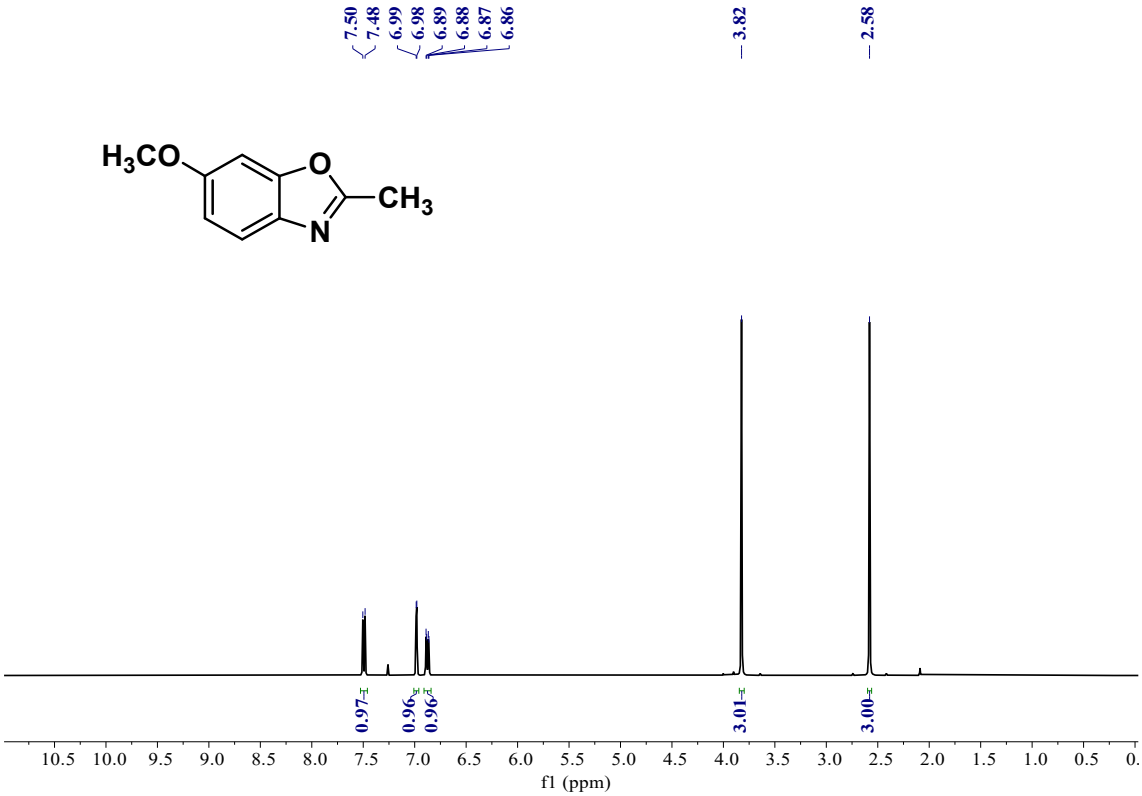
^{13}C NMR for product 3n (101 MHz, $CDCl_3$)



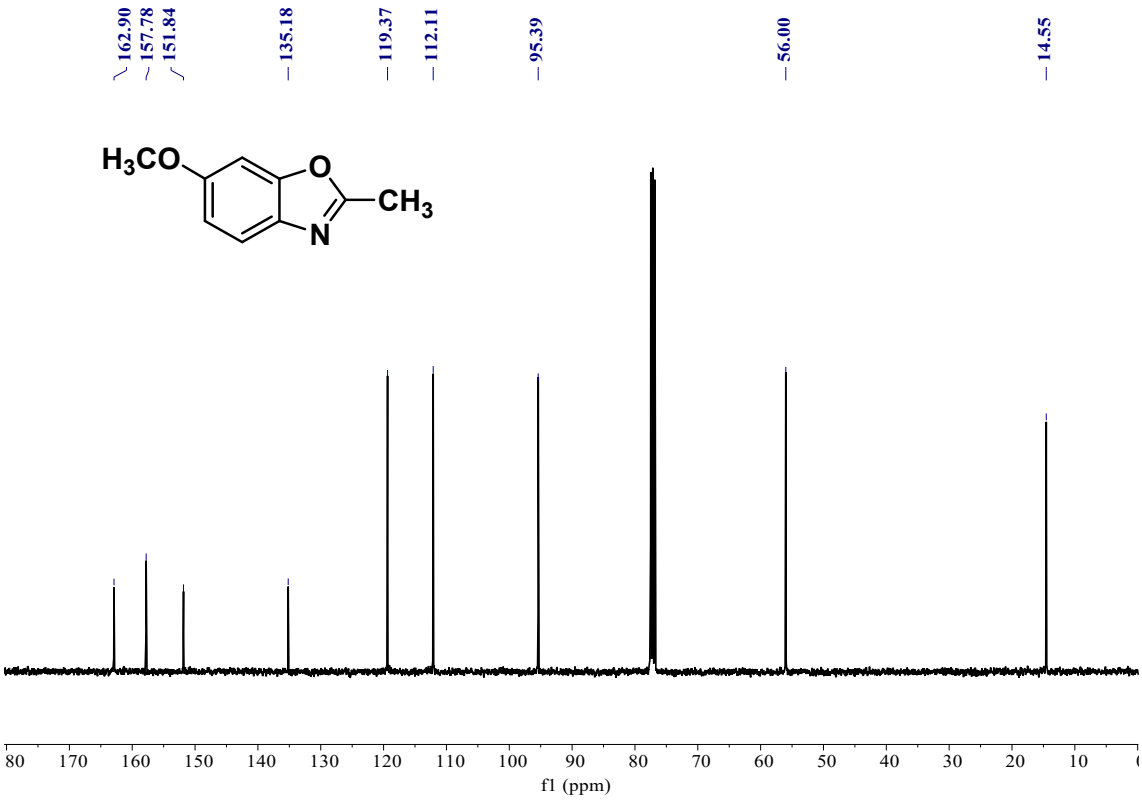
^{1}H NMR for product 3o (400 MHz, $CDCl_3$)



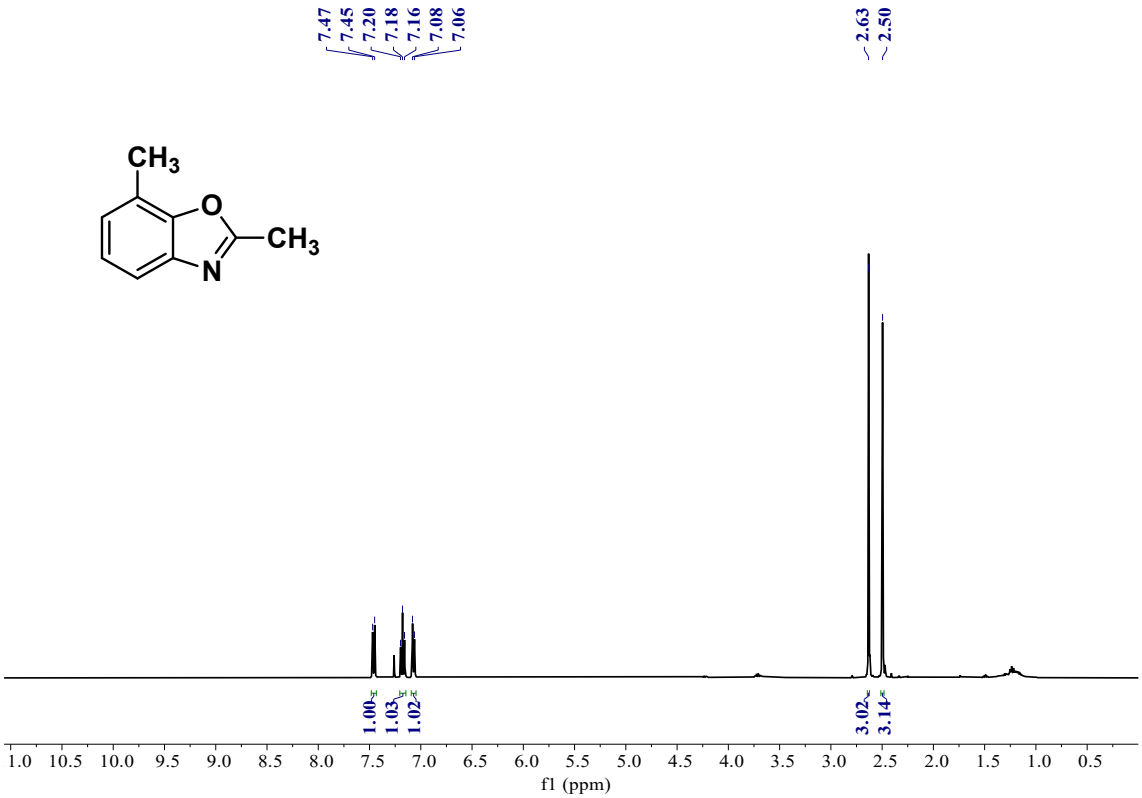
^{13}C NMR for product 3o (101 MHz, $CDCl_3$)



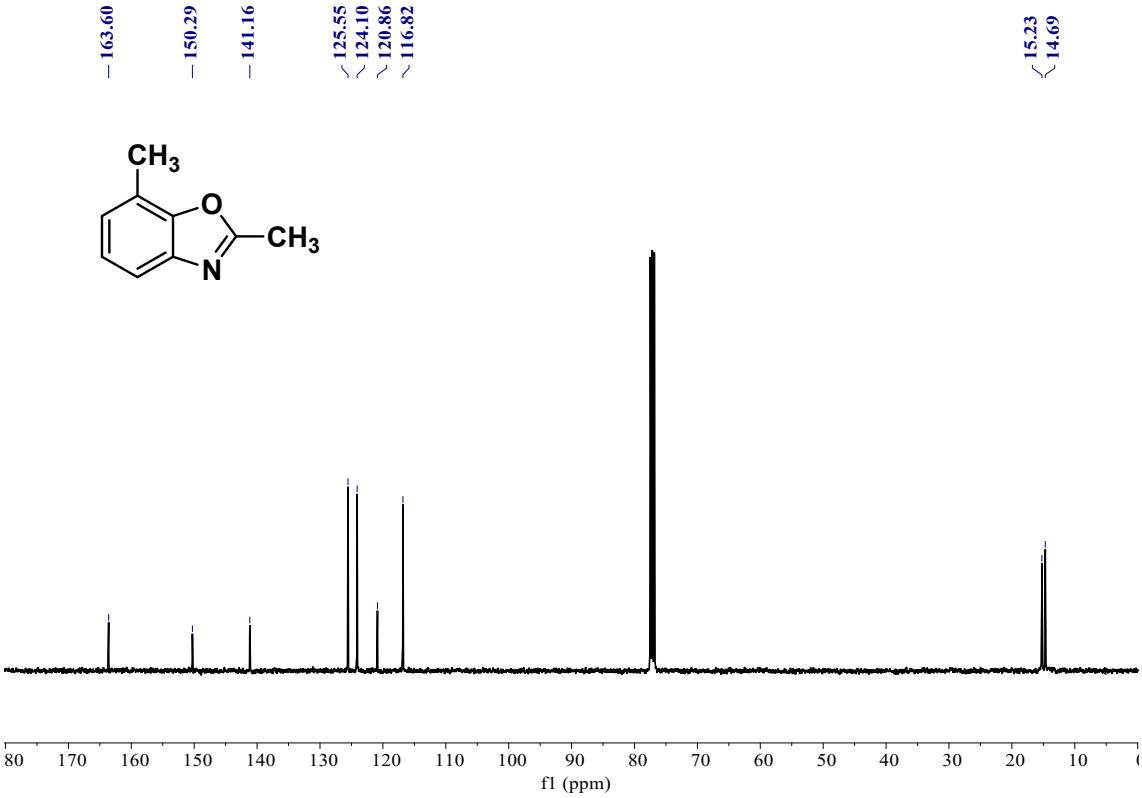
^{1}H NMR for product 3p (400 MHz, $CDCl_3$)



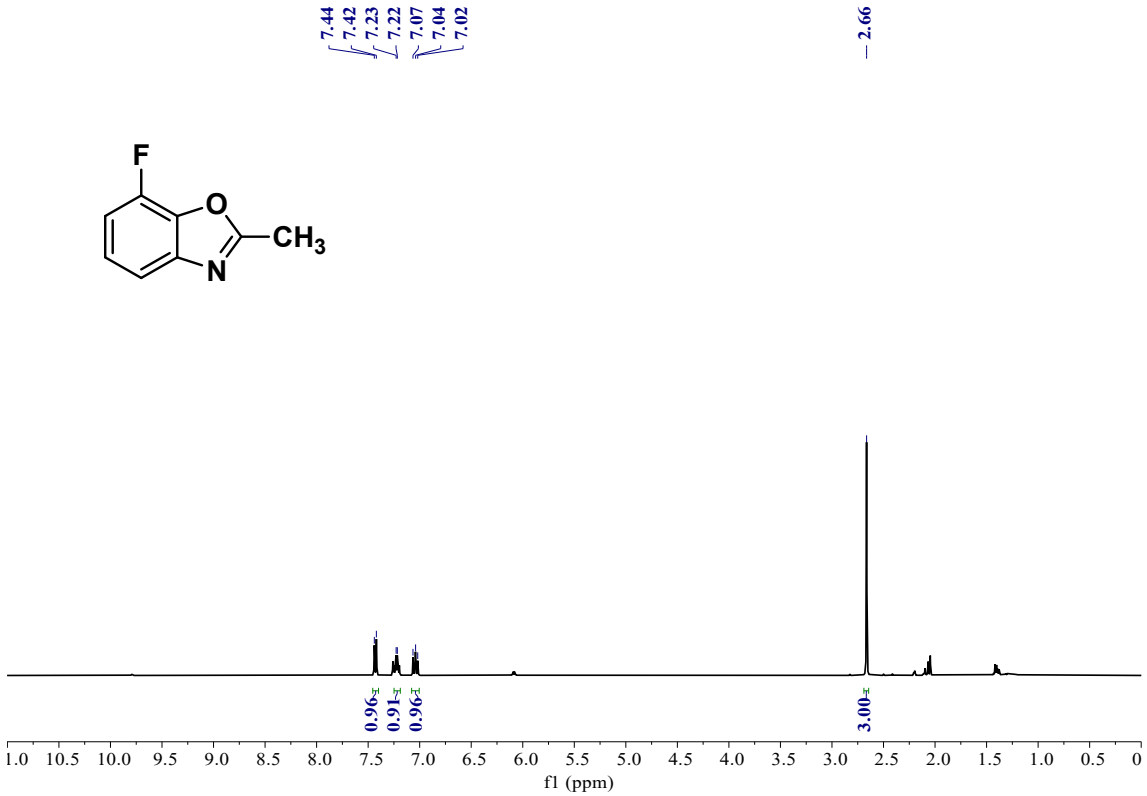
^{13}C NMR for product 3p (101 MHz, $CDCl_3$)



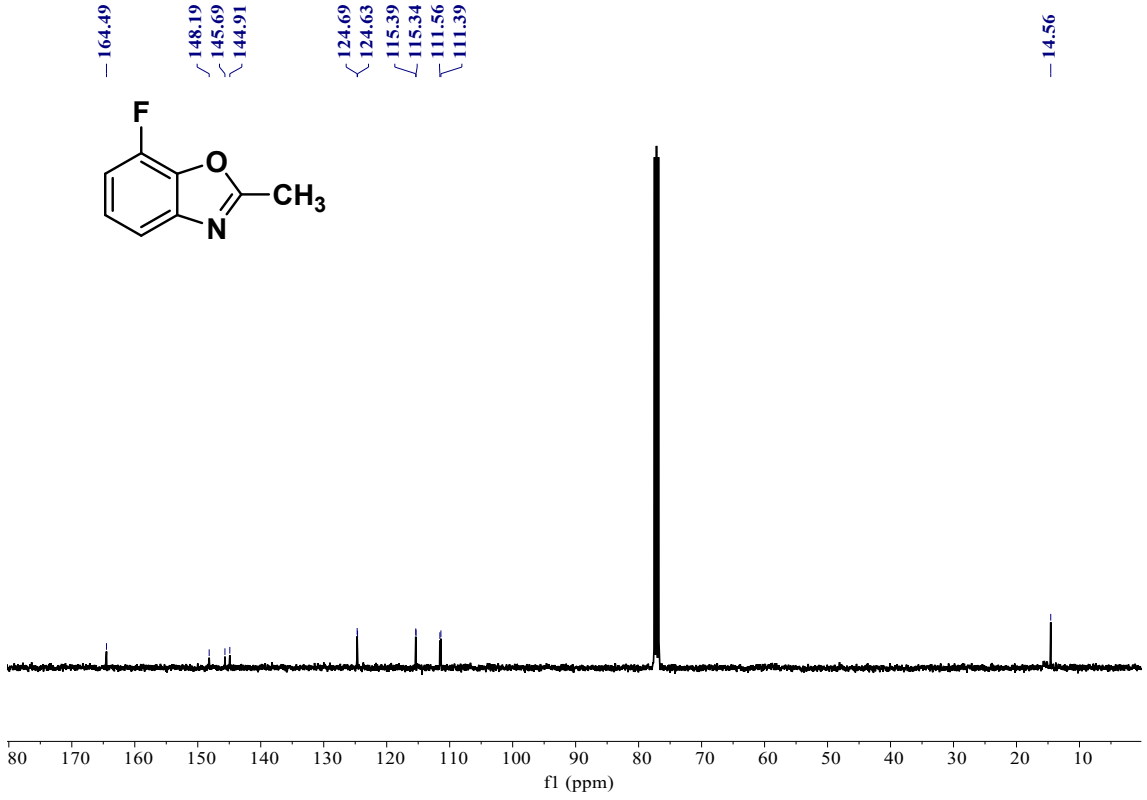
^{1}H NMR for product 3q (400 MHz, $CDCl_3$)



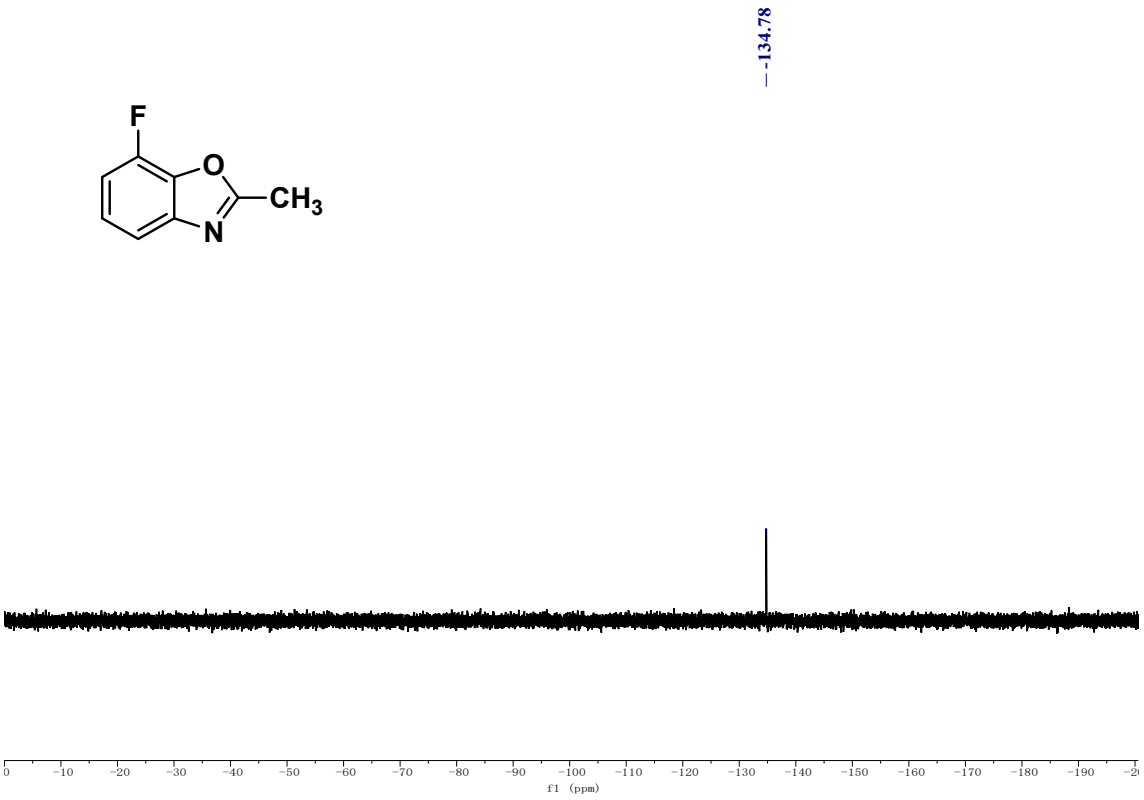
^{13}C NMR for product 3q (101 MHz, $CDCl_3$)



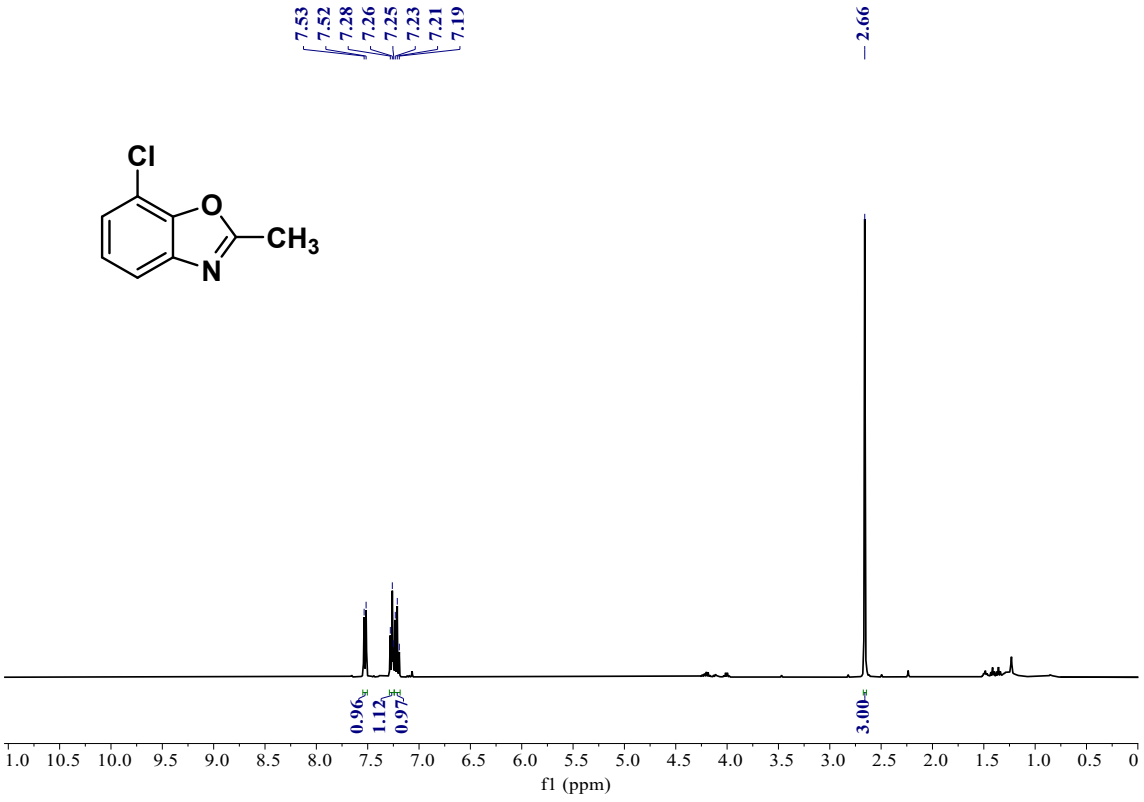
^{1}H NMR for product 3r (400 MHz, $CDCl_3$)



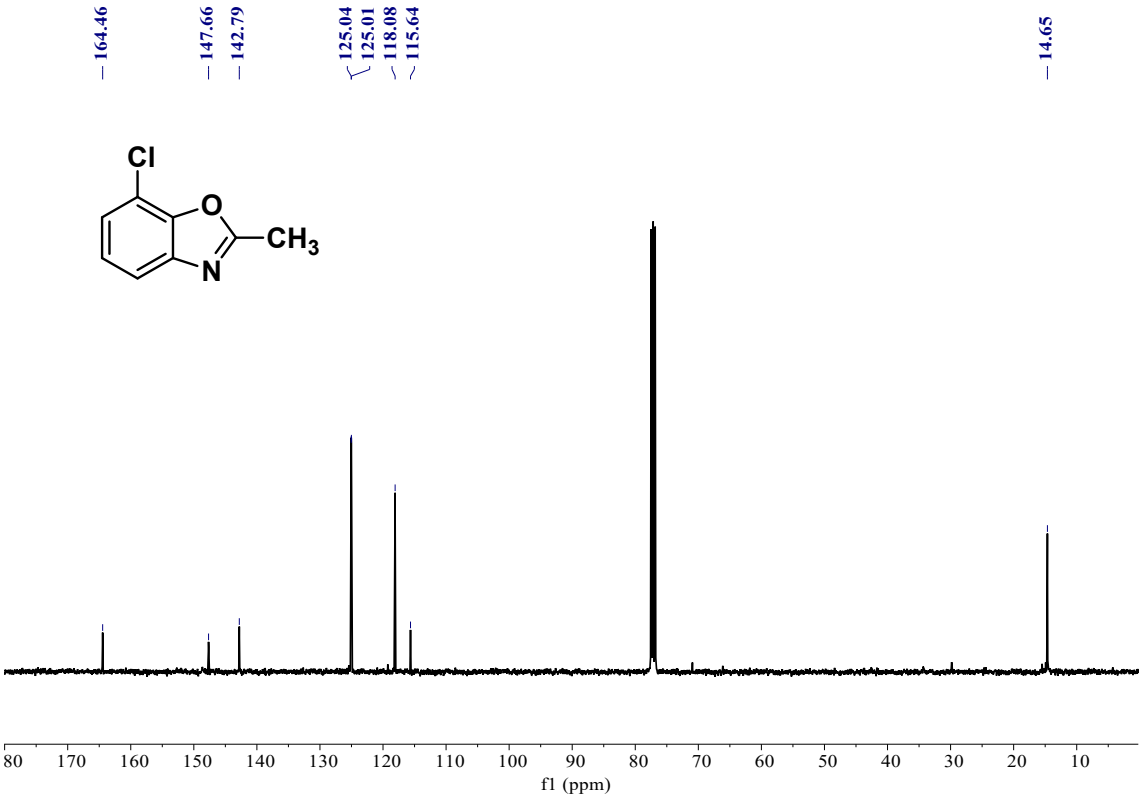
^{13}C NMR for product 3r (101 MHz, $CDCl_3$)



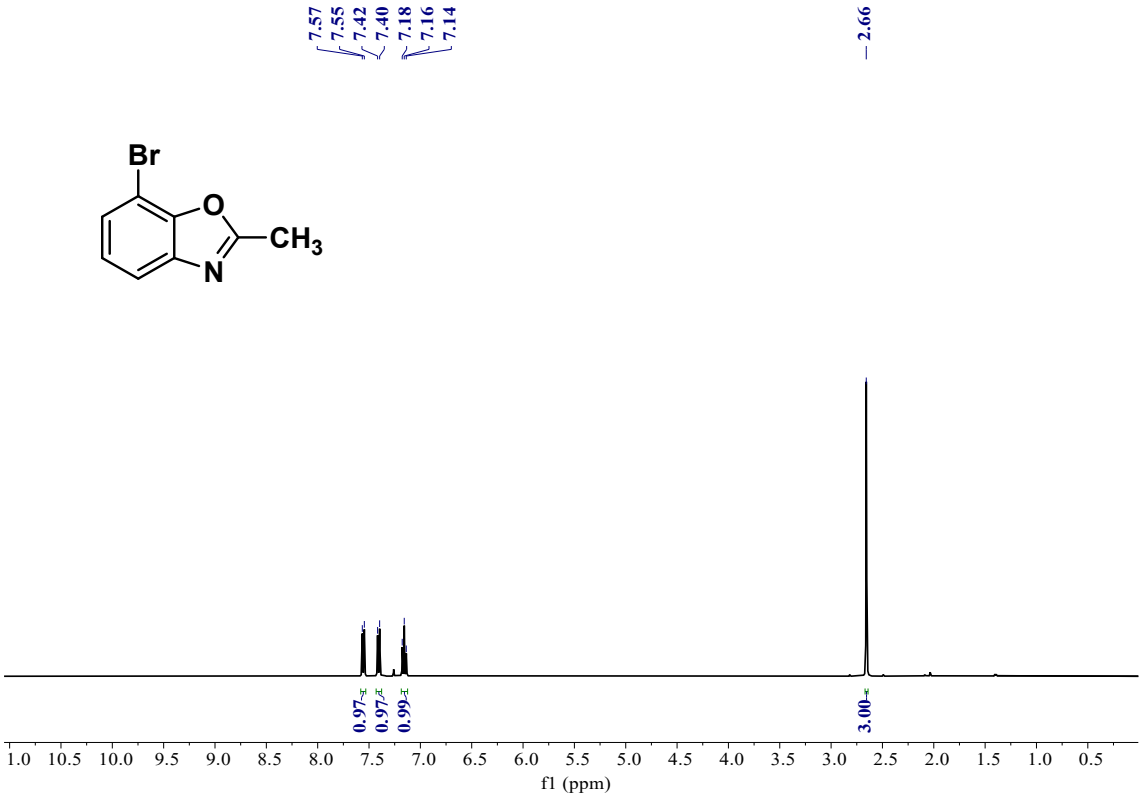
^{19}F NMR for product 3r (470 MHz, $CDCl_3$)



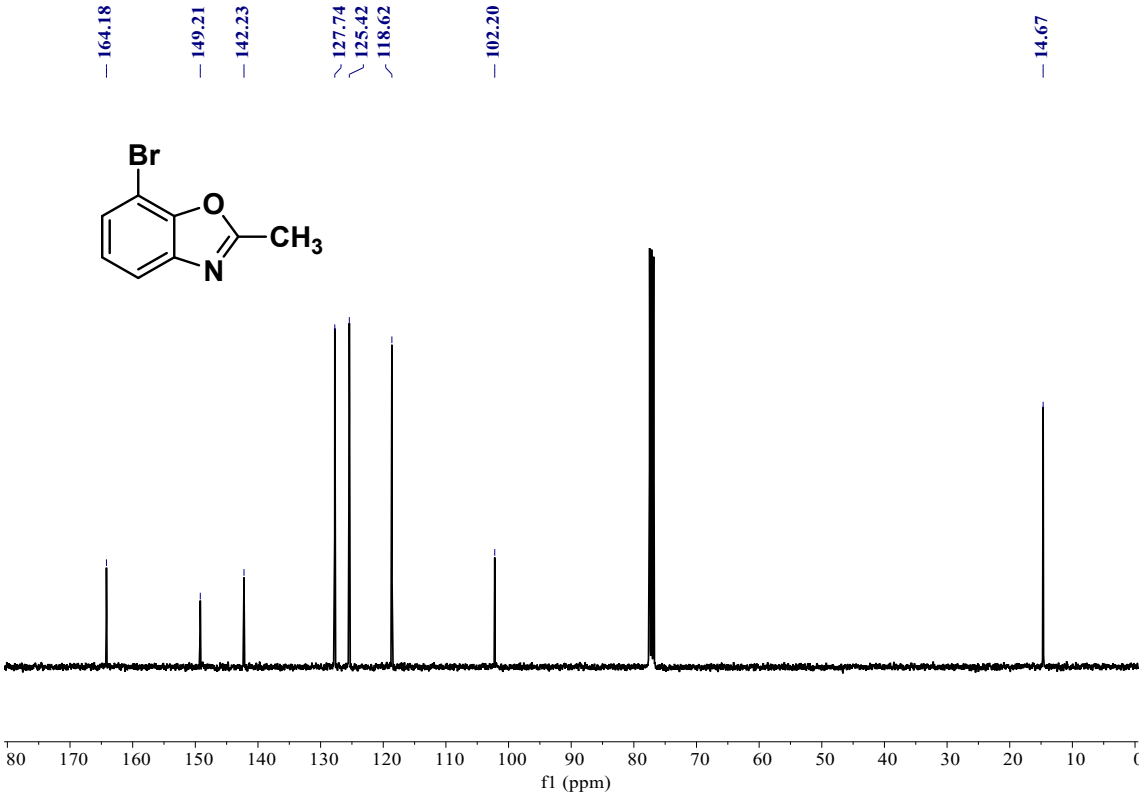
^{1}H NMR for product 3s (400 MHz, $CDCl_3$)



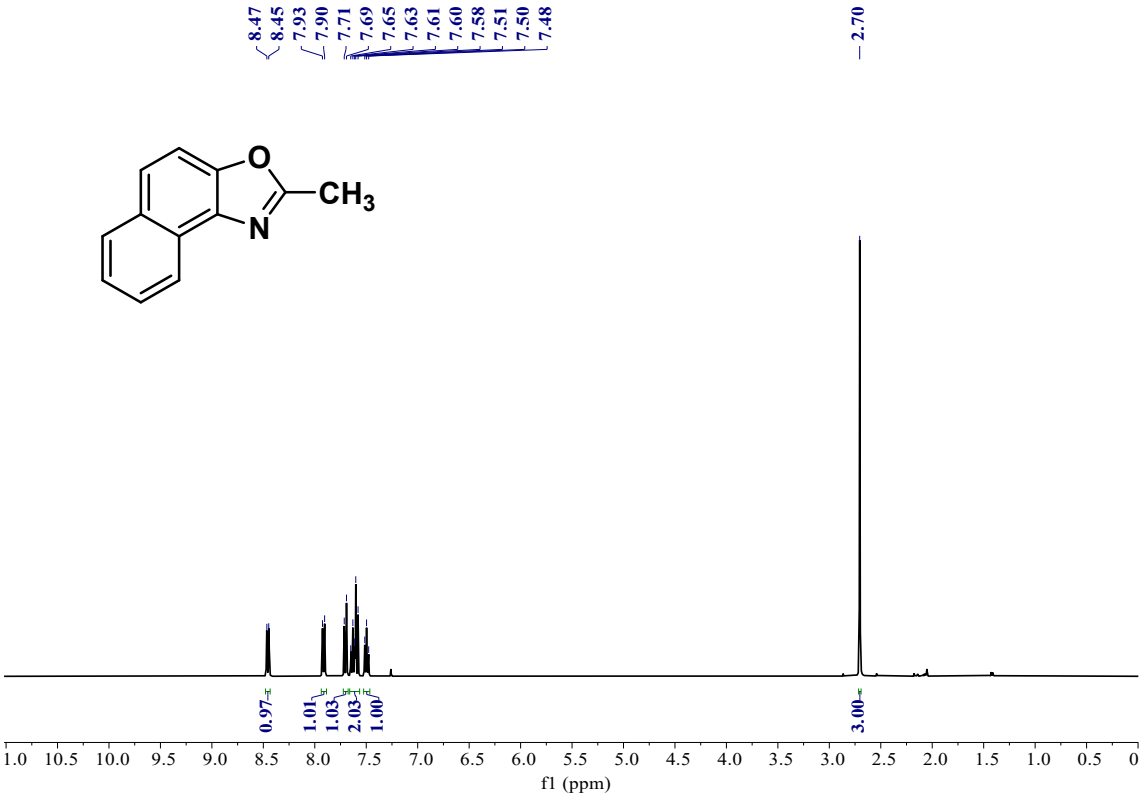
^{13}C NMR for product 3s (101 MHz, $CDCl_3$)



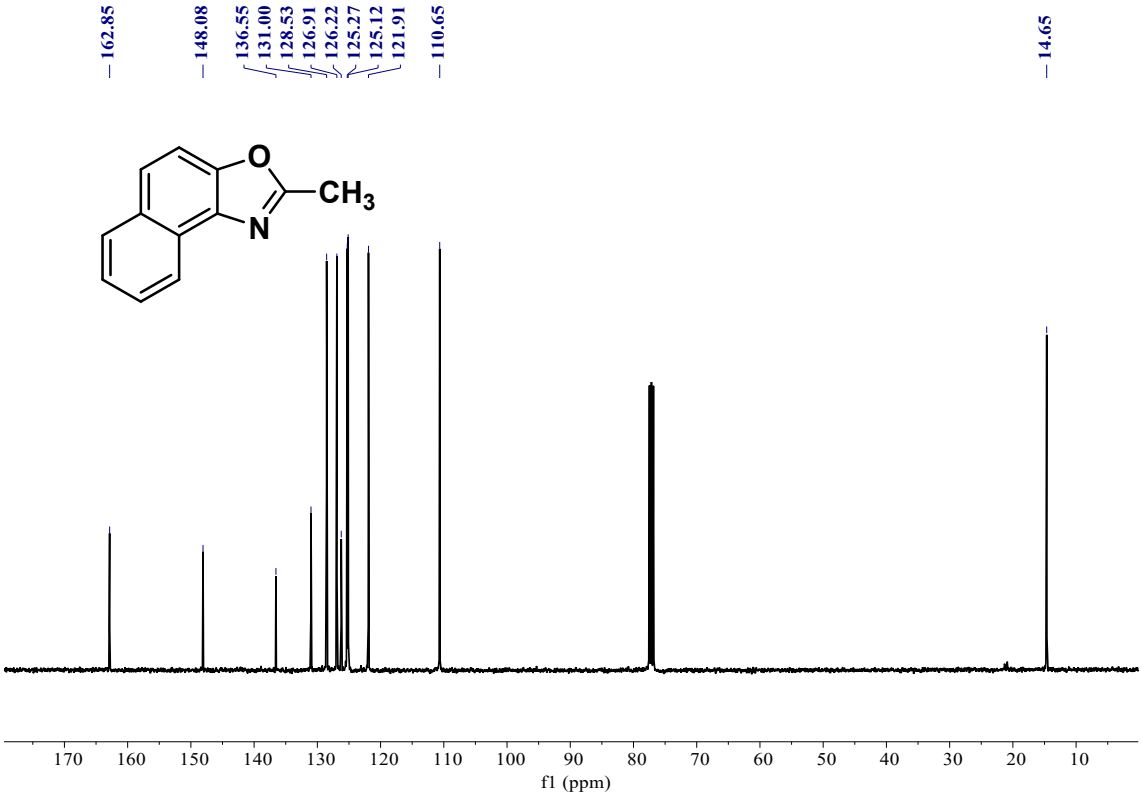
^{1}H NMR for product 3t (400 MHz, $CDCl_3$)



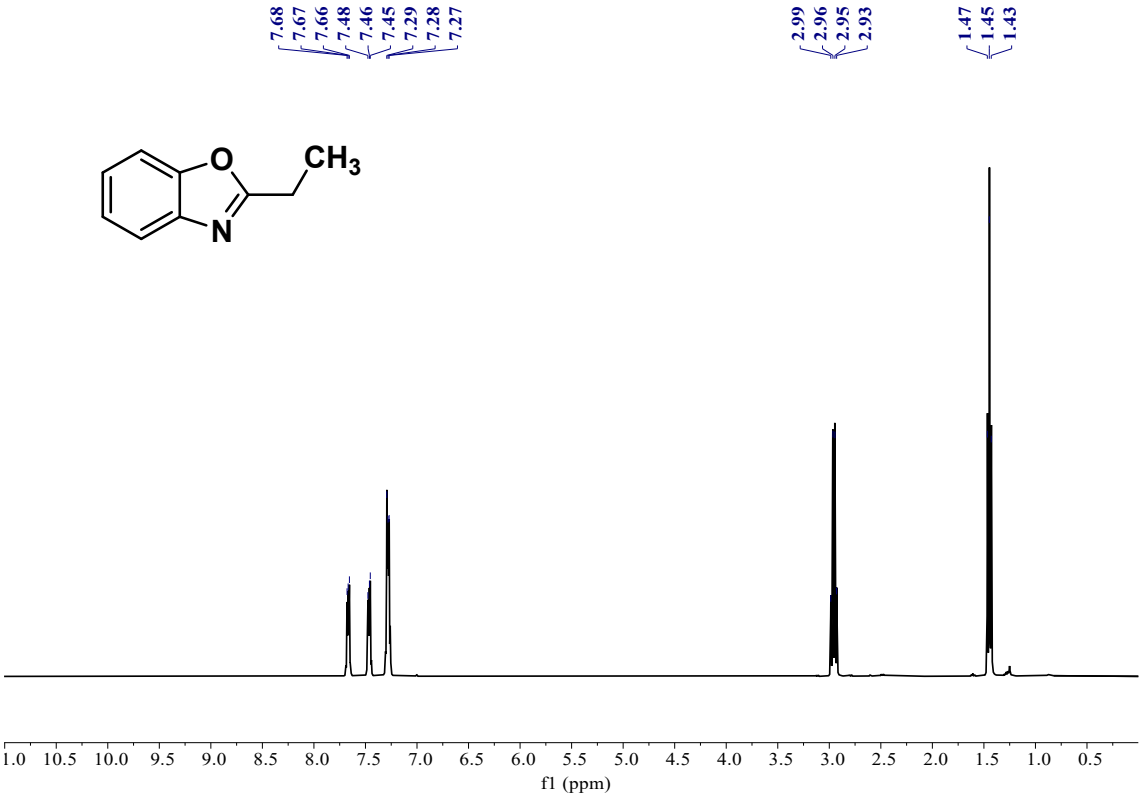
^{13}C NMR for product 3t (101 MHz, $CDCl_3$)



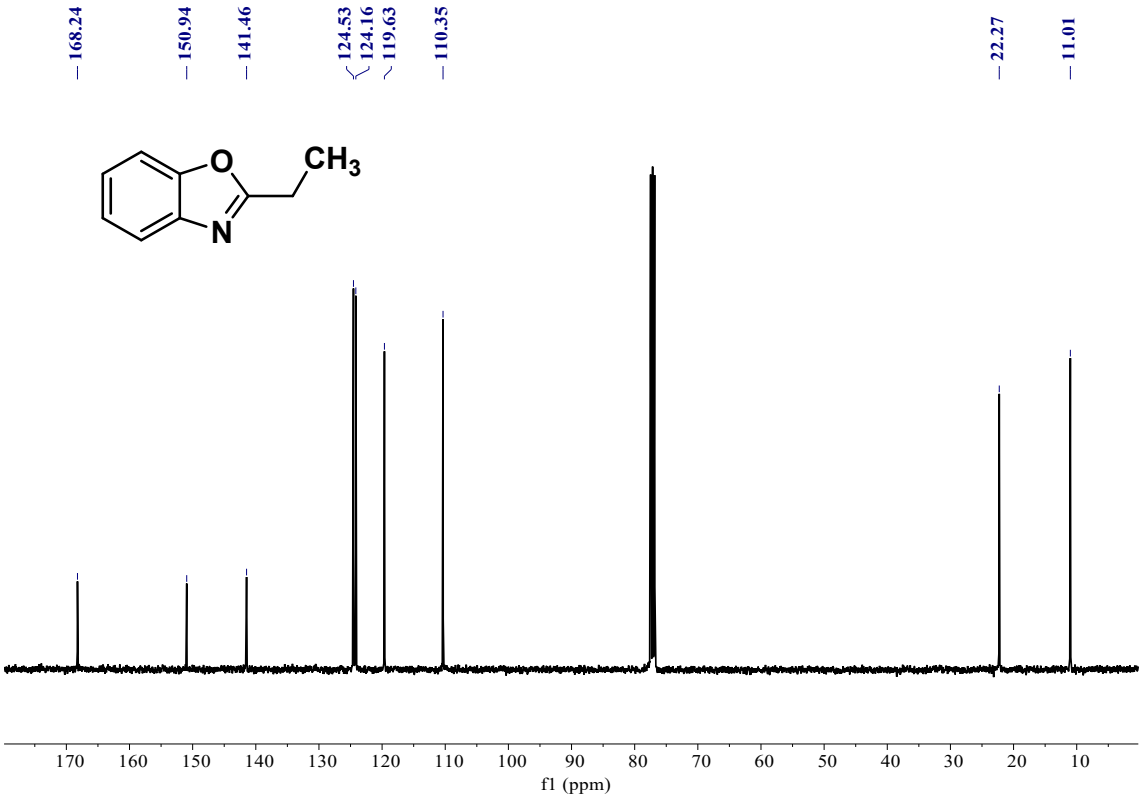
^{1}H NMR for product 3u (400 MHz, $CDCl_3$)



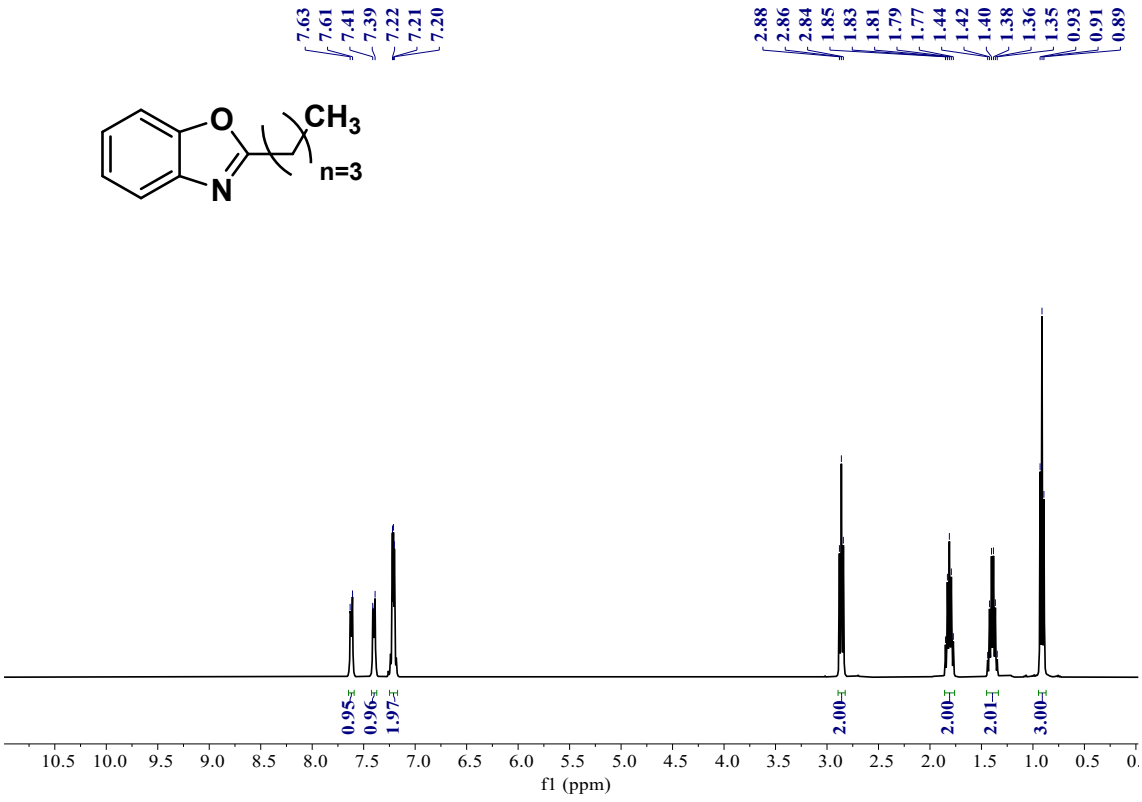
^{13}C NMR for product 3u (101 MHz, $CDCl_3$)



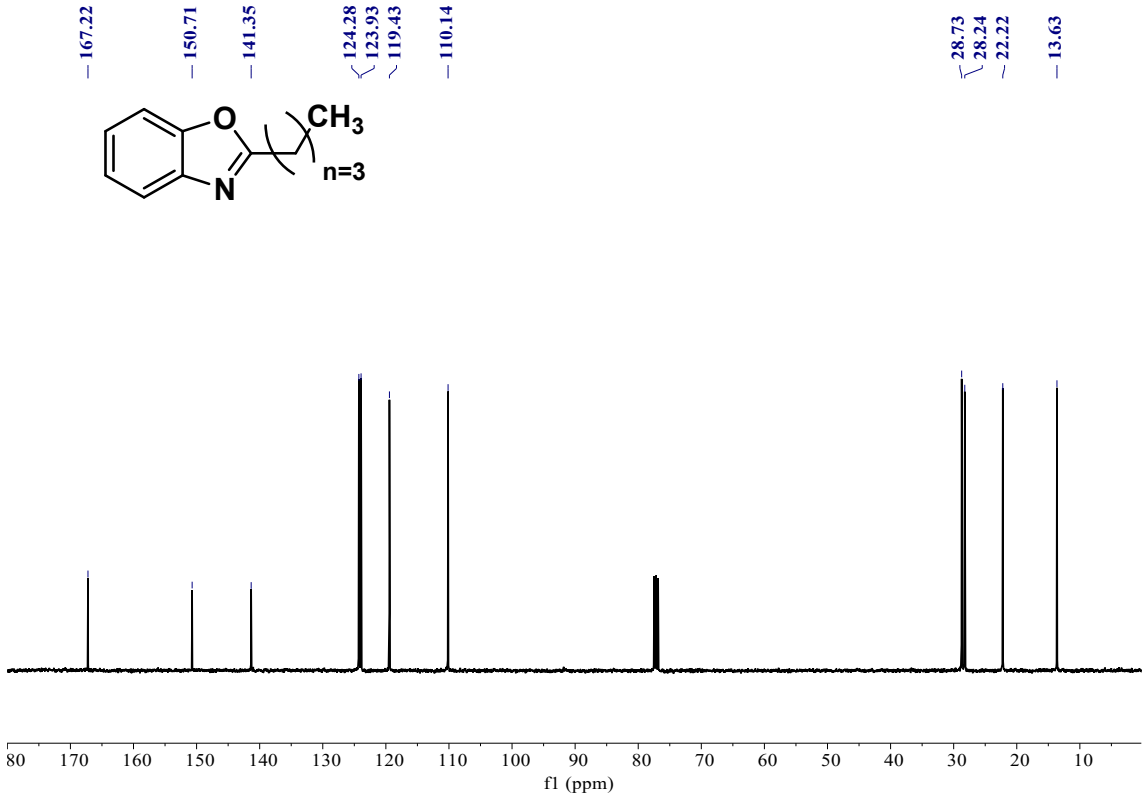
^{1}H NMR for product 3aa (400 MHz, $CDCl_3$)



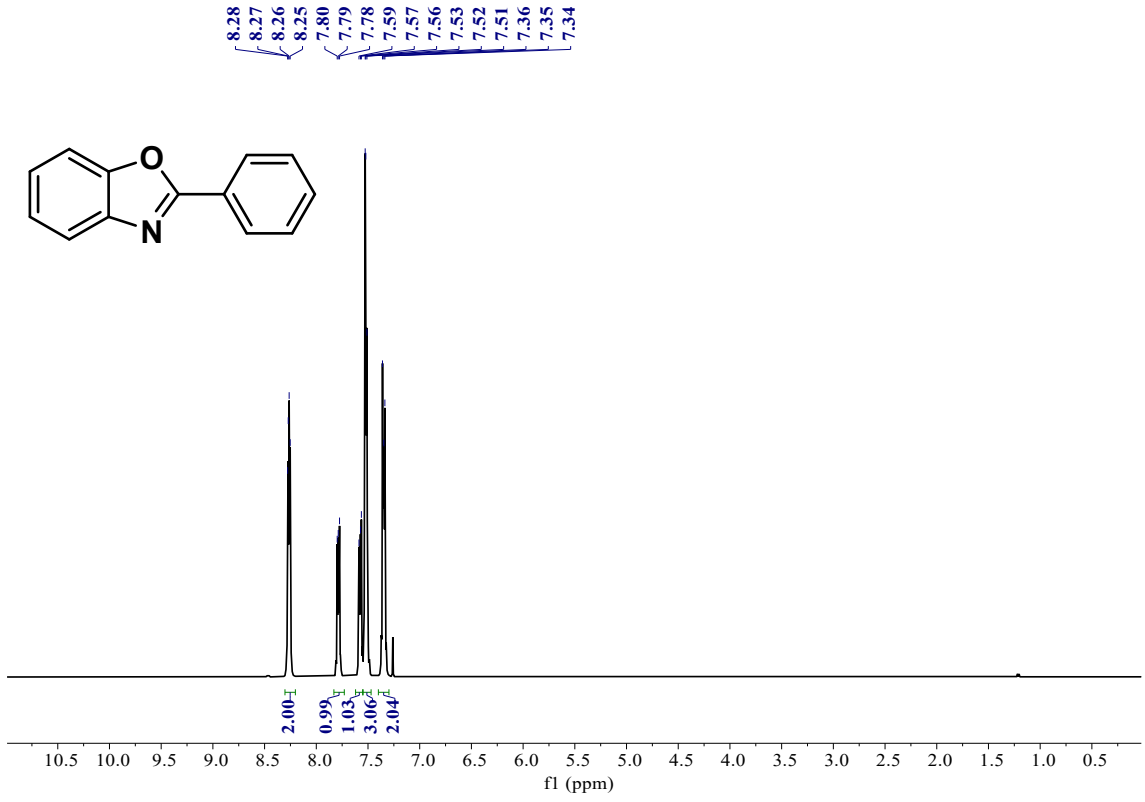
^{13}C NMR for product 3aa (101 MHz, $CDCl_3$)



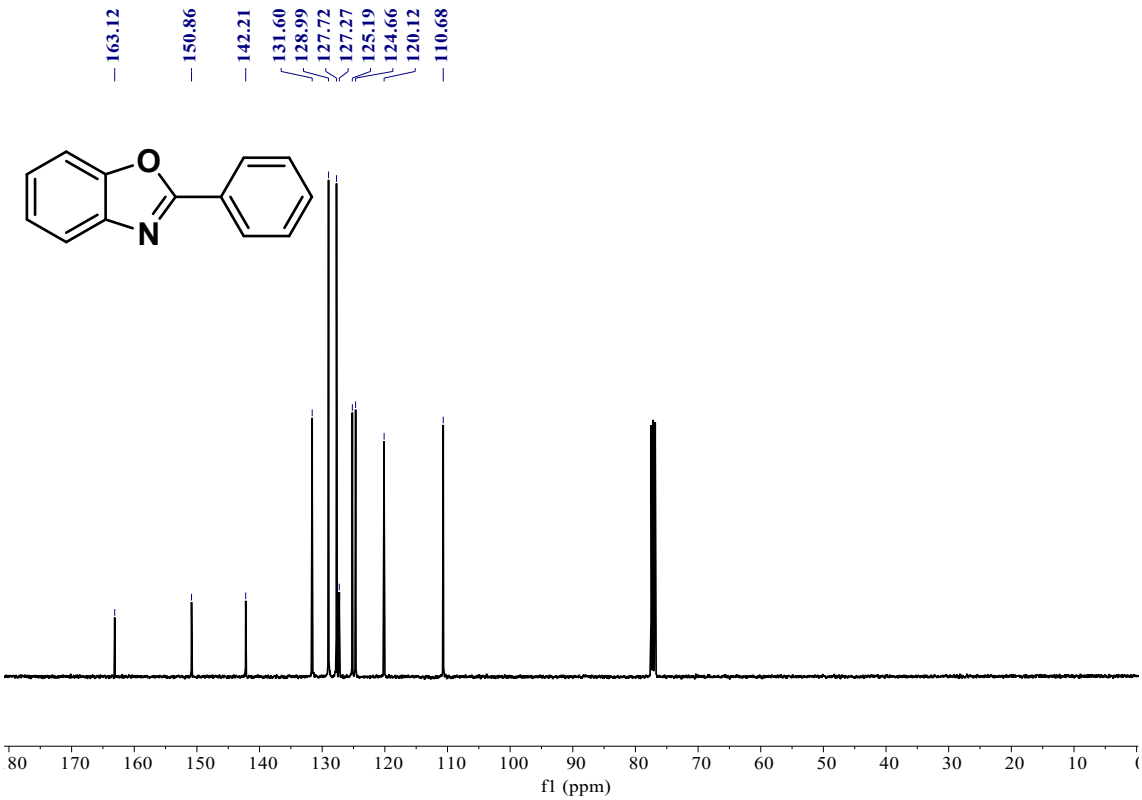
^{1}H NMR for product 3ab (400 MHz, $CDCl_3$)



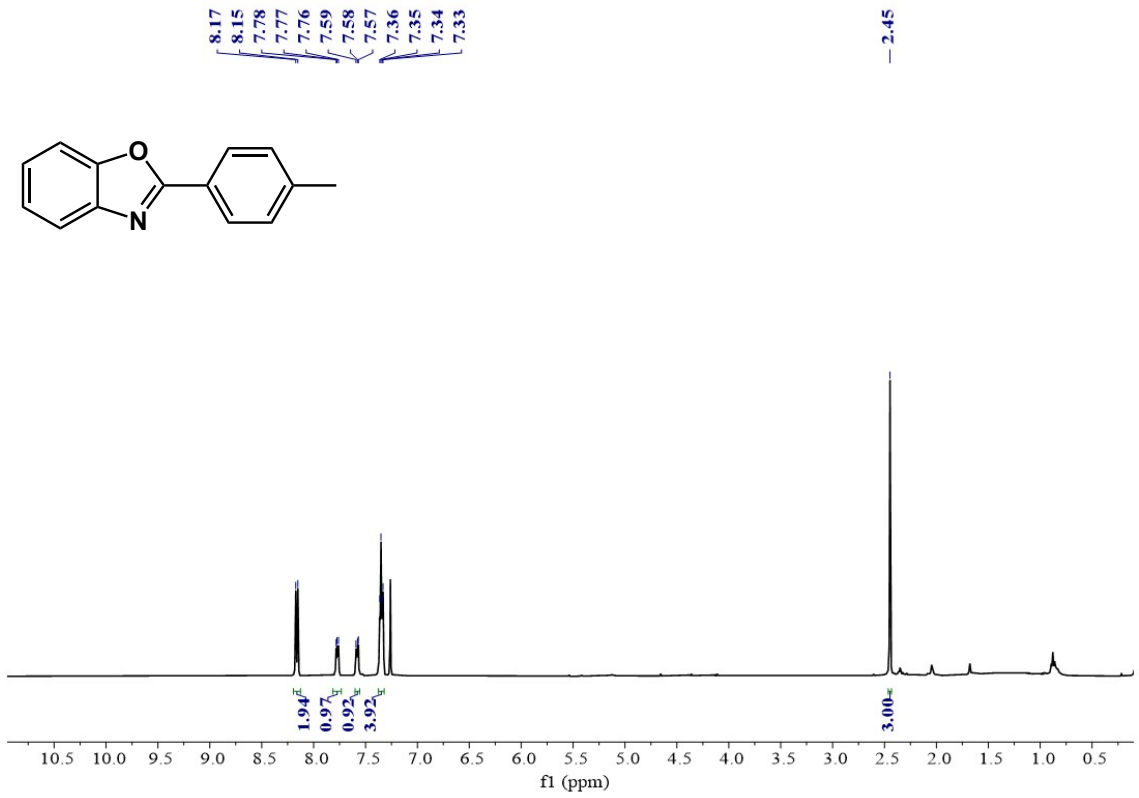
^{13}C NMR for product 3ab (101 MHz, $CDCl_3$)



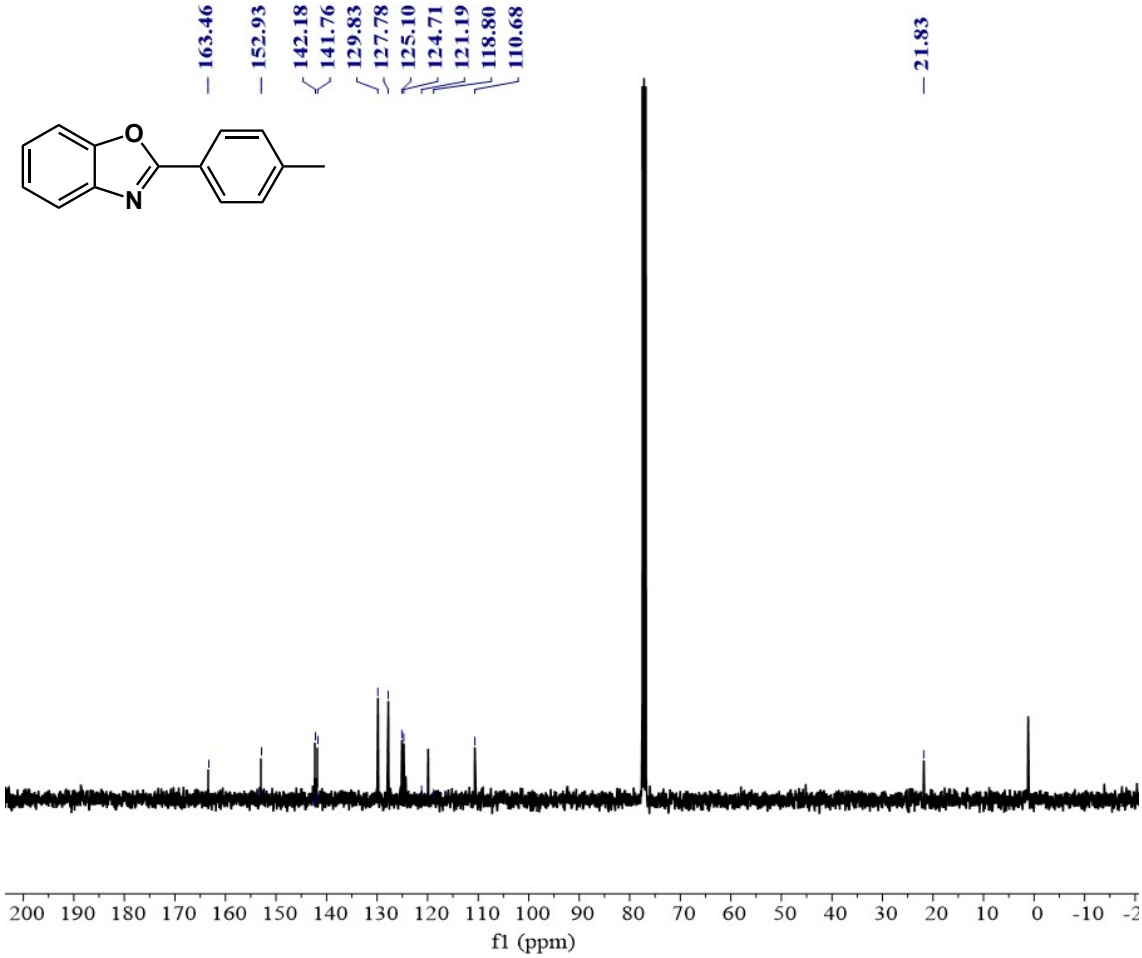
^{1}H NMR for product 3ac (400 MHz, $CDCl_3$)



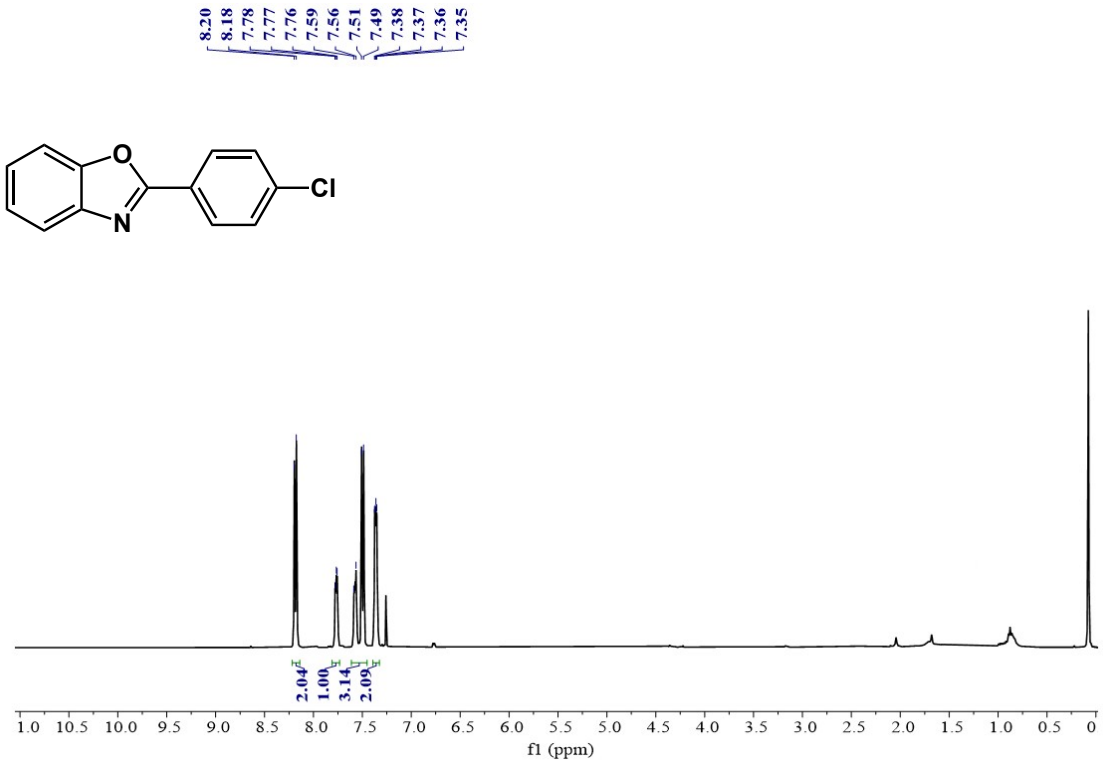
^{13}C NMR for product 3ac (101 MHz, $CDCl_3$)



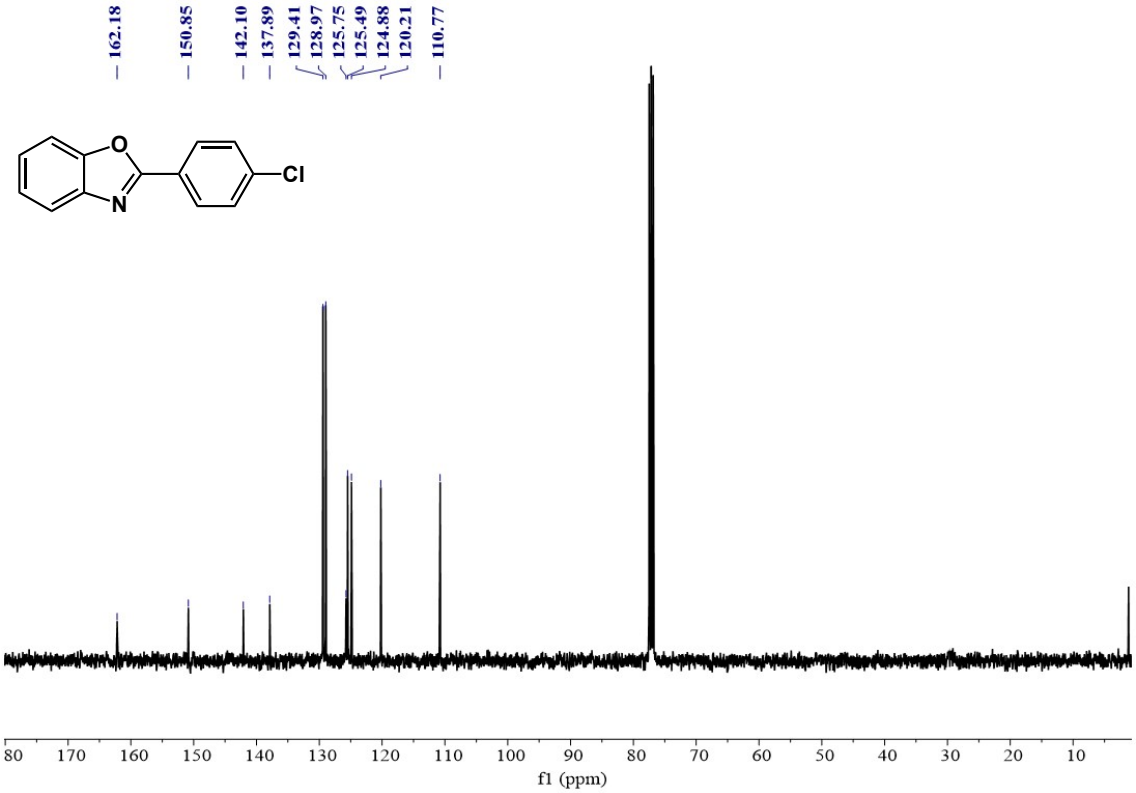
^{1}H NMR for product 3ad (400 MHz, $CDCl_3$)



^{13}C NMR for product 3ad (101 MHz, $CDCl_3$)



^{1}H NMR for product 3ae (400 MHz, $CDCl_3$)



^{13}C NMR for product 3ae (101 MHz, $CDCl_3$)

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